LV. *The Electronic Energy Levels of the Elements, with special reference to their Connexion with the Sizes and Electronic States of Atoms in Metallic Crystals. By* WILLIAM HUME-ROTHERY, *M.A., Ph.D.** [*]

I. INTRODUCTION.

IN a previous paper [1] the author has shown that to within an accuracy of about 1 per cent. some surprisingly simple relations exist between the interatomic distances in the crystals of the elements and the atomic numbers and electronic quantum numbers of the atoms concerned. The point of view adopted in that paper was that the size of the atom in the crystal is determined principally not by the valency electrons, but by the outermost shell of electrons of the atomic core or ion. Thus in the elements in the First Period the size of the atom was regarded as determined by the group of two electrons (the K electrons) for which the principal quantum number is 1, in the Second Period by the group of eight electrons (the L electrons) for which the quantum number is 2, and so on. As we shall explain later there are difficulties in this simple explanation, which led nevertheless to the

discovery of empirical relations for the interatomic distances, which fall into two classes as follows :—

(1) *The Law of the Sub-Groups,* according to which, if d be the interatomic distance in the crystal of the elements, Z the atomic number, and n the principal quantum number of the outermost shell of electrons remaining attached to the atomic core or ion, then for any one sub-group d is given by the relation

$$\frac{d}{n} = \left(\frac{1}{aZ}\right)^x,$$

where a and x are constants of which x is the same for groups in which the ions have the same electronic structures. It was shown further that for Groups I. A, II. A, and IV. A the value of x was almost $\frac{1}{3}$, so that the relations became approximately $\dfrac{d^3}{n^3} = \dfrac{1}{aZ}$. At the time the previous paper was written data were only available in the rare gas group (Group O) for the elements argon and xenon, so that it was impossible to test the linear relation between $\log\dfrac{d}{n}$ and $\log Z$ which the above equation requires, although it was shown that the line through the two points which were available had a slope of almost exactly $-\frac{1}{3}$, and was thus parallel to the corresponding lines for Groups I. A, II. A, and IV. A. Data are now available for neon [2] and krypton [3], and, as can be seen from fig. 1, the linear relation between $\log\dfrac{d}{n}$ and $\log Z$ is again confirmed. The best straight line through the four points corresponds to the equation

$$\frac{d}{n} = \frac{3\cdot597}{(Z)^{\cdot356}} = \left(\frac{1}{\cdot0275\,Z}\right)^{\cdot356},$$

and the deviations from linearity are of the order 1 per cent.

(2) *The Relations in the Periods* according to which the interatomic distances vary almost exactly as $\dfrac{1}{Z}, \dfrac{1}{Z^2}, \dfrac{1}{Z^3}$, and $\dfrac{1}{Z^5}$ for the elements at the beginning of the First, Second, Third, and Fourth Periods respectively.

These relations clearly suggest that the successive shells of electrons exert screening effects which vary periodically in an unexpectedly simple way, and in the present paper we shall show that similar relations can be traced for the electronic energy levels. We shall then make a detailed examination of the energy levels of the M and N electrons in the elements of the Third and Fourth Periods respectively, and shall show how these are related to the numbers of the electrons in the shell concerned. We shall then show that similar relations can be traced for the interatomic distances in the crystals of these

Fig. 1.
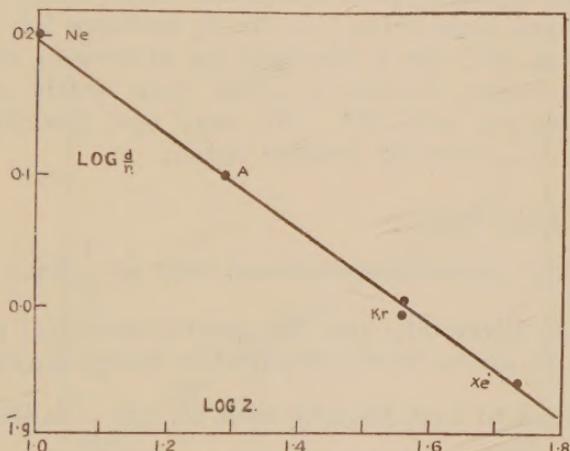
To illustrate the law of the sub-groups for the interatomic distances in the crystals of the elements of Group O (the Rare Gases). In

this figure $\log \frac{d}{n}$ is plotted against $\log Z$, where Z is the atomic

number, d the interatomic distance, and n the principal quantum number of the outermost shell of electrons in the atom. In the case of krypton the interatomic distance is 3·95 Å according to Keesom and Mooy (*Proc. K. Akad. Amsterdam*, xxxiii. p. 447 (1930)), and 4·04 Å according to Natta and Nasini ('Nature,' cxxv. p. 889 (1930)), and both values are included.

elements, and that the general correspondence between these empirical relations for the energy levels and inter atomic distances suggests a method for determining the state of the atom in the solid crystal.

II. The Relations in the Periods.

We have already explained how the relations for the interatomic distances in the crystals of the elements show that these vary as $\dfrac{1}{Z}$, $\dfrac{1}{Z^2}$, $\dfrac{1}{Z^3}$, and $\dfrac{1}{Z^5}$ at the beginning of the first four Periods respectively. We may summarize the correspondence between these relations and those found for the electronic energy levels by saying that when the interatomic distances vary as $\dfrac{1}{Z^x}$ at the beginning of a Period, the electronic energy levels vary linearly with Z^{2x} for the N_1 electrons of the outermost group of electrons of the atomic core or ion (*i.e.*, the 2_1 electrons for sodium, magnesium, etc., the 3_1 electrons for potassium, calcium), and this linear relation is often very nearly a direct proportionality with Z^{2x}. We may now describe these relations in somewhat greater detail.

(a) *The First Period.*

Here the interatomic distances vary as $\dfrac{1}{Z}$ from lithium to carbon (diamond), and the general empirical principle referred to above would require the energy levels of the K electrons to vary linearly with Z^2. If $\dfrac{\nu}{R}$ is the energy level term of the K electrons in the free atoms of the elements, it is of course well known that a linear relation exists between Z and $\sqrt{\dfrac{\nu}{R}}$, and a straight line is obtained by plotting $\dfrac{\nu}{R}$ against Z^2 as shown in fig. 2. This line does not pass exactly through the origin, so that the variation of $\dfrac{\nu}{R}$ is not accurately as Z^2—it is more usually written in the form $\sqrt{\dfrac{\nu}{R}} = Z - S$—but the deviation is comparatively slight, so that two or three adjacent elements—*e. g.*, beryllium, boron, and carbon—give points deviating but slightly from a line through the origin, so that the general correspondence between the interatomic

distances varying as $\dfrac{1}{Z}$ and the energy levels of the l_1 electrons as Z^2 is maintained although only as an approximation.

(b) *The Second Period*.

In this case the interatomic distances vary as $\dfrac{1}{Z^2}$ in sodium, magnesium, and silicon, the value for aluminium being greater because in this element the atoms are almost certainly not fully ionized in the solid crystal *. The

Fig. 2.
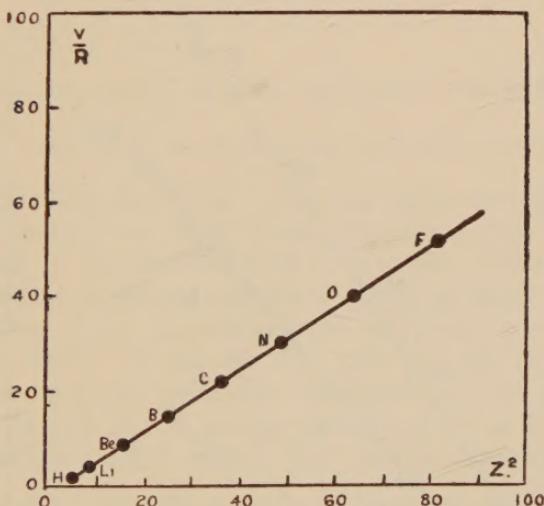
In this figure $\dfrac{\nu}{R}$ values for the K_1 electrons are plotted against Z^2 for the elements of the First Period.

general principle described above therefore leads us to expect the energy levels of the L_1 electrons to vary as Z^4, and in fig. 3 we have plotted the $\dfrac{\nu}{R}$ values for the L_1

* It may be noted that the abnormalities of aluminium in the sequence of melting points, electrical conductivities per atom, photoelectric threshold frequencies, etc., make it almost certain that this metal is incompletely ionized in the solid crystal, quite apart from the abnormal interatomic distances. This point may be emphasized, because the author fully realizes the undesirability of rejecting deviations from empirical relations unless the cause is quite certain.

and L_2 electrons against Z^4, the data being taken from the paper by Ray and Mukerjee [4], where these values are calculated accurately, and from the International Critical Tables, and it will be seen that where figures are available from both sources they are in good agreement except for the L_2 level in aluminium. The figure shows that for the L_1 levels the points lie almost exactly on a straight line through the origin as far as silicon, whilst the points

Fig. 3.
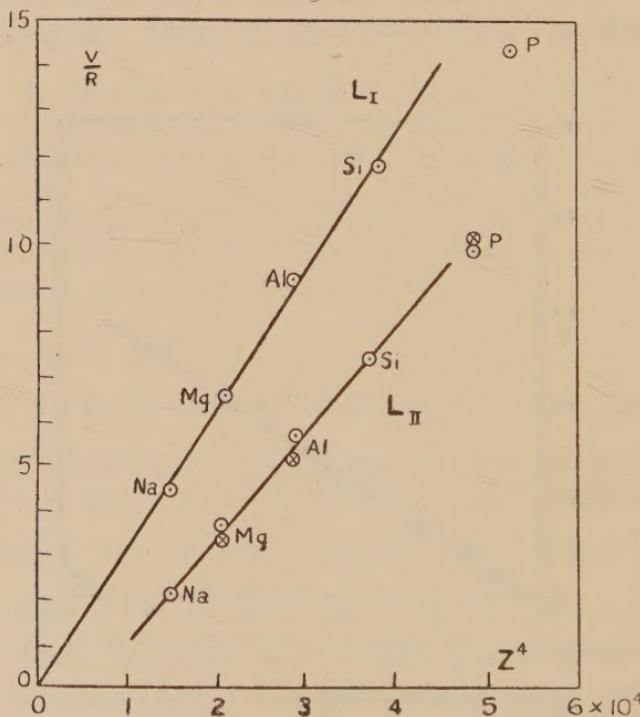
In this figure the $\frac{\nu}{R}$ values for the L_1 and L_{11} electrons are plotted against Z^4 for the elements at the beginning of the Second Period. The points marked ⊙ are from the data of Ray and Mukerjee, and those marked ⊗ from the International Critical Tables.

for the L_2 levels are also linear in Z^4 as far as silicon, although the straight line here does not pass through the origin. Each linear relation breaks down when we reach phosphorus, and it is of course well known that for the elements of somewhat higher atomic number the L_1 energy level terms follow a relation of the type

$$\sqrt{\frac{\nu}{R}} = a(Z - S).$$ There is thus no question of the linear

relation between $\frac{\nu}{R}$ and Z^4 being a general law extending

over a wide range of elements, but for the few elements at the beginning of the Second Period the relation is almost exact, and for the L_1 electrons the straight line passes directly through the origin in fig. 3, indicating a simple

proportionality between $\frac{\nu}{R}$ and Z^4. This clearly corre-

sponds empirically to the variation of the interatomic

distances as $\frac{1}{Z^2}$ at the beginning of this Period.

(c) *The Third Period.*

Here, as we have already explained, the interatomic

distances vary as $\frac{1}{Z^3}$ in potassium, calcium, and titanium,

in each of which the M shell contains eight electrons, since it is quite certain that these three elements are uni-, di-, and tetravalent in the solid crystal *. On the other hand in the free atoms of the elements the group of eight electrons only persists as far as calcium, the electronic structure of scandium being (2) (8) (9) (2), and not (2) (8) (8) (3). Using the general principle described above we shall therefore expect the M_I energy level to vary as Z^6 only as far as calcium, after which the process should become

more complex. In fig. 4 we have therefore plotted $\log \frac{\nu}{R}$

against $\log Z$ for both the M_I and M_{II} energy levels. For the M_I levels it will be seen that the slope of the line through the points for potassium and calcium is almost exactly 6/1, in complete agreement with expectation. Two points alone do not of course fix a line or a curve, but the slope of exactly 6 indicating a variation as Z^6 is clearly the counterpart of the slope of -3 corresponding to the varia-

tion of the interatomic distances as $\frac{1}{Z^3}$. During the

transition process which takes place between calcium and copper the line deviates, and we shall discuss these relations in detail in the next section, but it may be noted here

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* The structure of scandium has not yet been determined.

that when once the M shell has attained its full group of eighteen electrons at copper, the $\frac{\nu}{R}$ values for the M_I electrons increase almost exactly as Z^4 (*i. e.*, the slope of the log line is 4/1) until the second transition process begins at yttrium, where a slight deviation occurs. The data from the two sources are not in exact agreement,

Fig. 4.
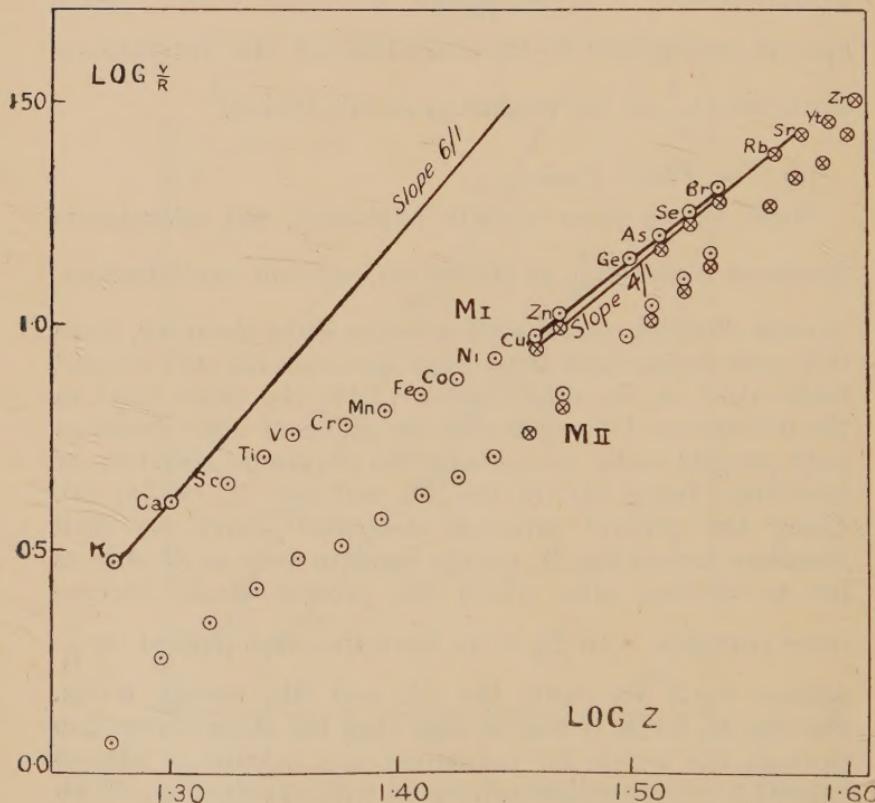
In this figure $\log \frac{\nu}{R}$ is plotted against $\log Z$ for the M electrons of the elements of the Third Period. The points marked ⊙ are from the data of Ray and Mukerjee, and those marked ⊗ from the International Critical Tables.

but each set of figures is consistent, and gives a slope of exactly 4/1.

The values for the M_2 electrons follow the same general type of variation, but the slopes of the lines are no longer

the exact whole numbers 6/1 and 4/1. The M_3 values are of course erratic, since the M_3 group only begins at scandium.

(d) *The Fourth Period*.

Here the interatomic distances vary nearly as $\dfrac{1}{Z^5}$ at the beginning of the Period, the exact slope of the line in the logarithmic diagram being $-5 \cdot 2$. In fig. 5 we have plotted $\log \dfrac{\nu}{R}$ against $\log Z$ for the N_1 and N_2 energy

Fig. 5.
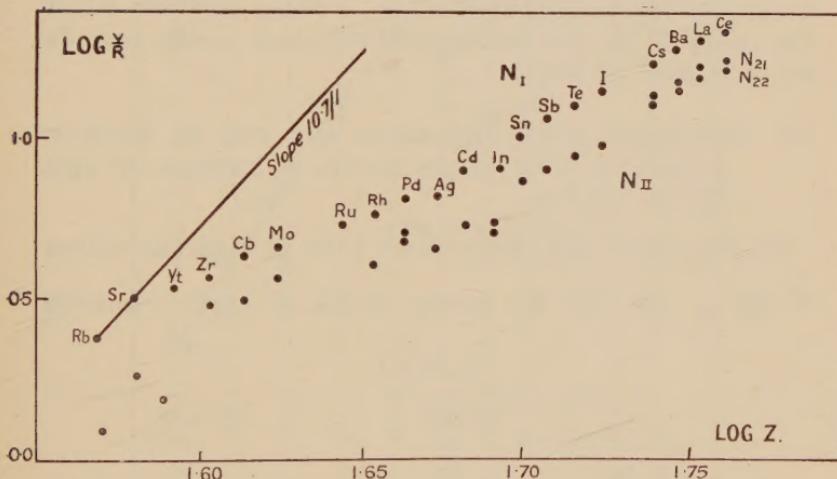
In this figure $\log \dfrac{\nu}{R}$ is plotted against $\log Z$ for the N electrons

of the elements of the Fourth Period.

levels, the data being taken from the International Critical Tables. It will be seen that the slope of the line through the points for rubidium and strontium is 10·7, or almost exactly double that in the diagram for the interatomic distances. As in the previous Period the transition process begins at Group III. A, so that the line of slope approximately 10 stops at the point for strontium. It will further be noted that, as in the preceding Period, after the transition process is complete at silver there is an approximately linear relation between the $\log \dfrac{\nu}{R}$ and $\log Z$ values for

the N_1 level, the slope being amost exactly 5/1. There are, however, one or two exceptions which may be due to errors in the data, since these are obviously irregular for the N_2 levels.

We may summarize these conclusions by saying that there is an almost complete correspondence between the relations found for the interatomic distances at the beginning of each Period and the values for the X_1 energy levels of the outermost shell of electrons of the atomic core or ion. Wherever the interatomic distances vary as $\dfrac{1}{Z_x}$, the energy levels of X_1 electrons vary as Z^{2x}. We shall show in the following section that this correspondence is maintained in an even more striking manner when the relations for the transitional elements of the periods are examined in detail.

III. THE INTERATOMIC DISTANCES AND THE M_I ENERGY LEVELS OF THE TRANSITIONAL ELEMENTS OF THE THIRD PERIOD.

In the upper half of fig. 6 we have plotted the values of $\log \dfrac{\nu}{R}$ for the M_I energy levels of these elements

TABLE I.

	M shell.	N shell.
K	8	1
Ca	8	2
Sc..............	9	2
Ti..............	10	2
V...............	11	2
Cr	13	1
Mn	13	2
Fe	14	2
Co	15	2
Ni	16	2
Cu	18	1

against $\log Z$, the scale being larger than in the preceding diagram. In order to understand these it is necessary to appreciate the way in which the transition process takes place, and we have therefore given in Table I. the numbers of electrons in the M shell (quantum

number 3) and the N shell (quantum number 4) in the free atoms of these elements. Potassium and calcium

Fig. 6.
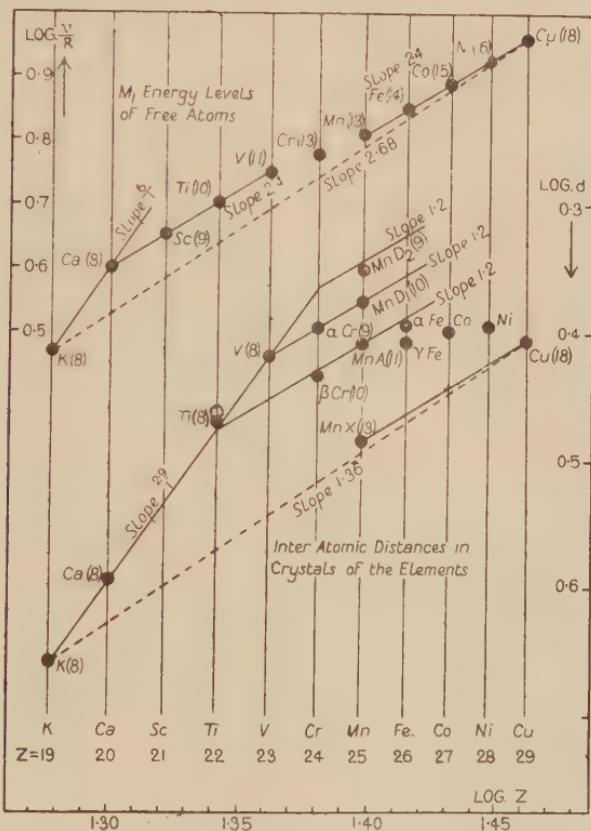
In the upper half of this figure $\log \frac{\nu}{R}$ is plotted against $\log Z$ for the M_I energy levels of the free atoms of the elements of the Third Period. In the lower half of the figure $\log d$ is plotted against $\log Z$, where d is the interatomic distance, *and the scale for $\log d$ is made double that for $\log \frac{\nu}{R}$, and reads downwards instead of upwards.*

In this way wherever lines are parallel in the two parts of the diagram, it implies that the slope in the lower diagram is minus one-half that in the upper.

The interatomic distance for cobalt is that of the face-centred cubic modification, and the same value is given by the a distance of approach in the close-packed hexagonal modification (axial ratio $c/a = 1·59$). It is for this reason that in the case of titanium, for which the axial ratio of close-packed hexagonal structure is also 1·59, the value considered and marked ● is the a distance of approach, and not the slightly smaller value marked O. This point is discussed in Section V.

both have eight electrons in the M shell, and, as can be seen from fig. 6, the M^1 energy level varies as Z^6 for these two elements. From calcium to vanadium successive steps result in the addition of one electron, not to the valency group but to the M_3 sub-group of the M shell. During this stage it will be seen that $\log \dfrac{\nu}{R}$ increases linearly with $\log Z$, the slope of the line being 2·4. At chromium, however, this regular process stops, the structures of chromium and manganese being (2) (8) (13) (1) and (2) (8) (13) (2) respectively, and there is a corresponding break in the line. From manganese to nickel the transition process again proceeds regularly, each step resulting in the addition of one electron to the M shell, and over this range the points again lie on a slope of approximately 2·4. On the other hand if the results of Ray and Mukerjee are accepted the point for copper lies almost exactly on this straight line in spite of the fact that there is a jump of two electrons in the M shell in passing from nickel [(2) (8) (16) (2)] to copper [(2) (8) (18) (1)]. As we have already seen in fig. 4 the values of Ray and Mukerjee are always a little higher than those from the International Critical Tables, but the difference between the two sets of figures is considerably greater in the case of copper (difference = ·35) than for the preceding metals, iron, nickel, and cobalt (differences ·05, ·008, ·28), so that it does not seem profitable to discuss this particular point in detail until the $\dfrac{\nu}{R}$ values are on a firmer basis. We may note further that the dotted line joining the points for potassium and copper has a slope of 2·68.

In view of the correspondence which we have previously found between the relations for the X_1 energy levels and those for the interatomic distances, it is natural to investigate the latter for these transition elements. For this purpose we have in the lower half of fig. 6 plotted $\log d$ against $\log Z$, and as we have previously found that a variation of $\dfrac{\nu}{R}$ as Z^{2x} corresponds to a variation of d as $\dfrac{1}{Z^x}$, we have doubled the vertical scale for $\log d$, and have made this read downwards instead of upwards. In this way wherever lines are parallel in the two figures it implies

that the slope in the lower diagram is minus one half that in the upper. We may now note our conclusions as follows, but it must be remembered that the differences in the coordination numbers (*i. e.*, the number of close neighbours which each atom possesses in the crystal) in the different types of crystal structure may be expected to affect the interatomic distances by amounts of the order 1 per cent.

(1) *Potassium, Calcium, Titanium, and Vanadium.*

The interatomic distances for all these elements lie on one straight line of slope almost exactly -3 (actual slope $= -2\cdot9$), as compared with the slope of $+6$ for the line through potassium and calcium in the energy level diagram in the upper half of the same figure. The most obvious conclusion here is that in the solid crystals of all these elements the M shell of eight electrons remains unchanged throughout.

(2) *The dotted line joining the points for potassium and copper* has a slope of $-1\cdot36$, as compared with $+2\cdot68$ (*i. e.*, $2 \times 1\cdot34$) in the diagram for the M_1 energy levels, so that the lines joining the points for the elements in Groups I. A and I. B have slopes which are almost exactly as 1 : 2. We may anticipate the next section by saying that both relations (1) and (2) are found for the elements of the Fourth Period, the gradients of the corresponding lines in the interatomic distance diagram again being exactly minus one half those in the energy level diagram, so that it is extremely improbably that this is a meaningless coincidence in the Third Period alone.

(3) *Chromium.*

This element crystallizes in two forms with widely differing interatomic distances, and the points for each modification are included in the diagram. It will be seen that the points for α chromium and vanadium lie on a line of gradient $1\cdot2$, or almost exactly minus one half the gradient of the lines in the upper diagram which correspond to the addition of one electron per step to the M shell. In view of the general empirical correspondence between the energy levels and interatomic distances, this clearly suggests that α chromium has nine electrons in the M shell, and we denote it therefore by the symbol Cr(9).

A similar parallel line passes very nearly through the points for titanium and β chromium, and since it is two steps from titanium to chromium, this clearly suggests that β chromium is Cr(10).

(4) *Manganese.*

The crystal structure of this element is highly complex, but in some ways the interatomic distances seem to fit in so well with the general type of variation described above, that the following interpretation is put forward tentatively.

In the very complicated structure of α manganese, the closest distance of approach is $2 \cdot 24$ Å, and when this is inserted in the diagram, it will be seen that it lies slightly below the point which would be indicated for Mn (9) by drawing a line of slope $1 \cdot 2$ through the point where the line through potassium, calcium, etc. cuts the ordinate for chromium. But the difference is only a little over 1 per cent. and may well be due to coordination effects.

The actual structure is, however, very complex. According to A. J. Bradley the structure may be described as of the body-centred cubic type in which each lattice point is replaced by a cluster of twenty-nine atoms. The structure contains atoms of four kinds which Bradley denotes X, A, D_1, and D_2 atoms, of which the D_2 atoms occupy the smallest volume and the X atoms the largest volume. Each X atom is surrounded by a cluster of four A and twelve D_2 neighbours, and outside these are the D_1 atoms.

In view of the existence of these four types of atoms in the structure, it seems natural to identify them with atoms in different states. We have therefore drawn lines of slopes $1 \cdot 2$ through the points where the line through the points for potassium, calcium, etc. cuts the ordinates for titanium and vanadium, and from the intersection of these lines we predict the values for Mn (10) and Mn (11) to be $2 \cdot 37$ Å and $2 \cdot 57$ Å respectively. Further by drawing a line in the lower part of the diagram parallel to the line which joins the points for Cu(18) and Mn(13) in the upper energy level diagram, we predict the value for Mn(13) as $3 \cdot 06$ Å. We now suggest tentatively :

(1) That Bradley's X atoms are Mn (13), for which we predict $d = 3 \cdot 06$ Å.

(2) That the A atoms are Mn (11), for which $d = 2\cdot57$ Å.

(3) That the D_1 atoms are Mn (10), for which $d = 2\cdot37$ Å.

In order to justify the procedure we must show first that the predicted values give the correct interatomic distances in such a way that each atom touches at least one neighbour, and secondly that no two atoms in the structure are closer together than our values require.

The following table is taken from Bradley's paper :—

<div align="center">

TABLE II.

Interatomic Distances of α Manganese.

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No. of neighbours.	D_2 atoms. Type of neighbours.	Distance.	No. of neighbours.	D_1 atoms. Type of neighbours.	Distance.
1..........	D_2	2·24	1..........	D_2	2·45
2..........	D_2	2·38	1..........	A	2·49
1..........	D_1	2·45	2..........	D_2	2·51
2..........	D_1	2·51	2..........	D_2	2·66
	X atoms.			A atoms.	
12..........	D_2	2·71	3..........	D_1	2·49
4..........	A	2·82	3..........	D_2	2·69
			1..........	X	2·82

According to an interpretation we have therefore :

$$X = 3\cdot06 \text{ Å}, \qquad D_1 = 2\cdot37 \text{ Å},$$
$$A = 2\cdot57 \text{ Å},$$

and we accept Bradley's value of $2\cdot24$ Å for D_2.

For the A atoms we expect therefore

    A to $X = \frac{1}{2} (3\cdot06 + 2\cdot57) = 2\cdot815$ as compared with the experimental $2\cdot82$ Å.

    A to $D_1 = \frac{1}{2} (2\cdot58 + 2\cdot37) = 2\cdot475$ Å as compared with the experimental $2\cdot49$, and for A to D_2 if in contact $\frac{1}{2} (2\cdot57 + 2\cdot24) = 2\cdot405$, and no D_2 atom is closer to A than this.

For the X *atoms we expect*

>   X to A $= 2 \cdot 815$ Å in good agreement with experiment as explained under A.

>   X to $D_2 = \frac{1}{2} (3 \cdot 06 + 2 \cdot 24) = \overline{2 \cdot 65}$ Å, the experimental value $(2 \cdot 71$ Å) being greater than this by an amount which may be due to coordination effects, or may indicate that these atoms are just not in contact. Whilst for X to D_2, and X to X the experimental values are much greater, indicating that these are not in contact.

For the D_1 *atoms we expect*

> D_1 to A $= 2 \cdot 475$ Å in good agreement with experiment as explained above, whilst for D_1 to D_2, D_1 to D_1, and D_1 to X the experimental values are all much greater, showing that these are not in contact.

For the contact of two D_2 *atoms* we have assumed Bradley's value $2 \cdot 24$ Å, and the experimental values for the distances D_2 to A, and D_2 to D_1 are greater than our values require, indicating that these are not in contact, whilst the case of D_2 to X has been discussed above.

It can be seen therefore that the whole scheme hangs together in a most remarkable way. Each of the three values we have deduced from our diagram finds its appropriate place in the complex structure of α manganese, whilst the fourth value taken from Bradley's results for the size of the D_2 atoms differs from that required by the diagram for Mn (9) by an amount of the order of the co-ordination effect.

The second allotrope of manganese (β manganese) has been investigated by Preston [6], and the closest distance of approach is $2 \cdot 365$ Å, which is almost exactly the value of $2 \cdot 37$ Å which we predicted for Mn (10) and identified with the D_1 atoms in α manganese. Unfortunately it does not yet seem possible to predict from fig. 6 the values for Mn (12) which appear to be required in order to account for the remaining interatomic distances; for if the upper part of this diagram referring to the energy levels be examined, it will be seen that there is a very distinct

break in the regular process after the M shell contains eleven electrons, and consequently whilst it is reasonable to draw the line from the point for Ti (8) in order to give the value for Mn (11), it does not appear justifiable to draw a corresponding line through the point for Sc (8) in order to give the value for Mn (12).

Finally, in the third allotrope of manganese (α manganese) examined by Westgren the closest distance of approach is 2·585 Å, which is very nearly that (2·57 Å) which we predicted for Mn (11), but again it does not seem justifiable to speculate on the value for Mn (12).

It must of course be admitted frankly that the methods used above are purely empirical, and we shall discuss their limitations later, but the general correspondence between the two halves of the diagram can hardly be dismissed as mere coincidence, particularly as the same general type of relation is also found in the next period.

(5) *Iron, Nickel, and Cobalt.*

From the remarks made in connexion with the interatomic distances in manganese, it will be appreciated that it is unjustifiable to draw lines through the points for potassium, calcium, scandium, and titanium in order to predict values for atoms in states such as Fe (12), Co (14), Ni (15), etc., and we have therefore included the points for these three elements without the corresponding lines. It will be noted that the relation between the points for Mn (11) and α Fe in the interatomic distance diagram is very much like that existing between V (11) and Cr (13) in the energy level diagram, suggesting that α Fe is Fe (13), but we are here dealing with very small differences, and it does not appear advisable to discuss the point in detail, since the difference between the interatomic distances in the α and γ iron is only of the order 1 or 2 per cent., and may well be due to the pure coordination effects of the different types of structure, and not to the existence of atoms in different states. In view of the marked increase in interatomic distances on passing from nickel to copper, we may tentatively suggest the structures Cu (18), Ni (15) [or (16) ?], or Co (14) [or (15)?], and Fe (13) or (12), but these cannot be looked upon as conclusive, although they can hardly be wrong by more than one electron if the correspondence between the two diagrams is not mere coincidence. It is clear that the break between

(11) and (13) is one at which there is comparatively little difference between neighbouring states, and it is significant that in the interatomic distance diagram the metal iron with its abnormal ferromagnetic properties comes just at this point.

IV. The Interatomic Distances and the N_1 Energy Levels of the Transitional Elements of the Fourth Period.

In view of the marked correspondence between the diagrams for the M_1 energy levels and interatomic distances in the elements of the Third Period, we have in fig. 7 drawn a similar diagram for the N_1 energy levels and interatomic distances for the elements of the Fourth Period. This diagram is constructed in exactly the same way as that in (4), and the scale for log d is again inverted and made double that for $\log \dfrac{\nu}{R}$.

The details of the two diagrams are however slightly different, and in order to understand these it is necessary to consider the transition process in the free atoms, the electronic structures of which are given in Table III. :—

Table III.

Rb	(28)	(8)	(1)
Sr	(23)	(8)	(2)
Yt	(28)	(9)	(2)
Zr	(28)	(10)	(2)
Nb	(28)	(12)	(1)
Mo	(28)	(13)	(1)
Ma	(28)	(14)	(1)
Ru	(28)	(15)	(1)
Rh	(28)	(16)	(1)
Pd	(28)	(18)	(0)
Ag	(28)	(18)	(1)

From this it will be seen that, as in the Third Period, the transition process begins in Group III. (Yt). But whereas in the Third Period the transition process proceeded uniformly so that at each step one electron was added to the M shell as far as vanadium, after which a

break occurred, in the Fourth Period the break occurs after zirconium in Group IV. The second point is that whilst rhodium and silver have outer groupings of (16) (1) and (18) (1) respectively, palladium departs from this regular process and has a structure (18) (0). This is clearly revealed in the diagram for the N_1 energy levels. From rubidium to strontium we have a straight line of slope

Fig. 7.
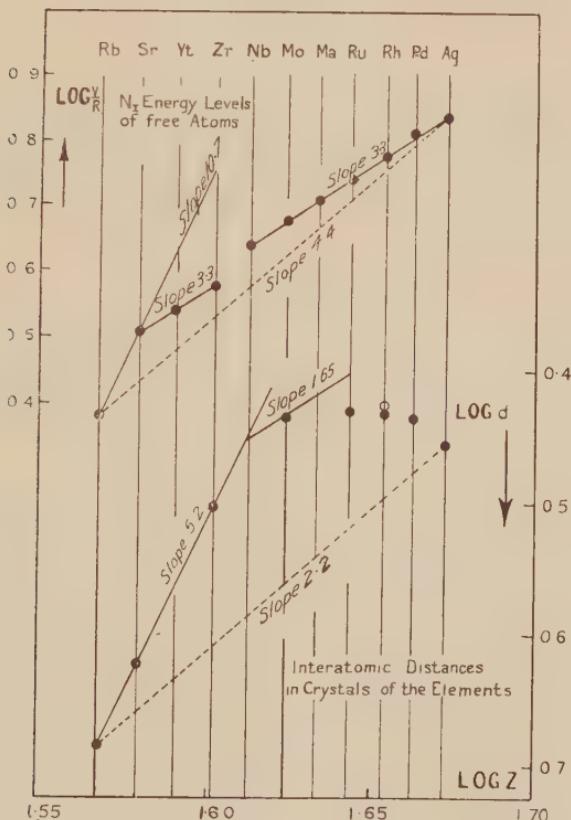
In the upper half of this figure log $\frac{\nu}{R}$ is plotted against log Z for the

N_I energy levels of the elements of the Fourth Period. In the lower half of the diagram log d is plotted against log Z, and, as in the

preceding diagram, *the scale of log d is double that of log $\frac{\nu}{R}$ and*

reads downwards instead of upwards. As in the previous figure, it is the a distances of approach which are marked ● in the close-packed hexagonal metals zirconium and ruthenium.

2 X 2

10·7 as compared with 5·2 in the figure for the lattice constants. From strontium to zirconium, and from niobium to silver the points for the N_1 energy levels lie on straight lines of slope 3·3, but the single point for palladium deviates as it should do *. The dotted line joining the points for silver and rubidium has a slope of 4·4.

As in the previous figure we have drawn an interatomic distance diagram in which the scale for $\log d$ is halved, and is made to read downwards, and the following points may now be noted :

(*a*) The points for rubidium, strontium, and zirconium all lie on one straight line of gradient 5·2 as compared with the gradient 10·7 for the line between rubidium and strontium in the energy level diagram. Presumably therefore the group of eight electrons remains unchanged in these elements.

(*b*) The dotted line joining the points for rubidium and silver has a slope of −2·2, as compared with 4·4 for the corresponding line in the energy level diagram, so that as in the Third Period the general correspondence between the points at the beginning and end of the Period is maintained.

(*c*) Data are not available for niobium in Group V., but if we produce the line through the points for rubidium, strontium, and zirconium, so as to give the point for a hypothetical Nb (8), it will be seen that the line joining this point with that for the experimental value for molybdenum in Group VI. has a slope of 1·65, or exactly one half the slope of the lines in diagram for the N_1 energy levels. This is precisely the same kind of relation as that found in the Third Period, and the correspondence can hardly be a coincidence. The conclusion is presumably that in the solid crystal the structure is Mo (9).

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* It may be objected here that if the $\frac{\nu}{R}$ value for copper is incorrect, the line in the lower half of fig. 6 may be taken as giving the value of Mn (14) by analogy with fig. 7, and not Mn (13). The important point is that the line of gradient 1·2 through the point for copper gives the correct value for MnX in fig. 6, and until the $\frac{\nu}{R}$ values are entirely certain it does not seem possible to decide this conclusively.

(*d*) Data are not available for masurium in Group VII., so that the relations analogous to those found for manganese cannot be tested in the Fourth Period, whilst the marked break in the regular process which occurs between the points for Zr (10) and Nb (12) in the energy level diagrams clearly makes it unjustifiable to extrapolate more than two places from the line corresponding to structures with eight electrons in the N shell. For this reason it does not appear advisable to discuss in detail the points for ruthenium, rhodium, and palladium, although in view of the increased steepness of the lines, and the wider angles produced by the transition process in fig. 7 as compared with fig. 6, it seems probable that the structures of ruthenium, rhodium, and palladium are analogous to those of iron, cobalt, and nickel.

Unfortunately in the next Period the figures for the O energy levels given in the International Critical Tables are so erratic that it does not seem justifiable to discuss their relation to the interatomic distances.

V. Some Energy Level Relations in the Sub-Groups.

In the preceding sections we have seen that the relations found for the interatomic distances in the elements of any one Period are duplicated by a series of relations for the energy levels in such a way that a variation of the interatomic distance as $\dfrac{1}{Z^x}$ is accompanied by a variation of the X_1 energy level as Z^{2x}, where X_1 refers to the outermost group of electrons in the atomic core of iron. It seemed therefore of interest to see whether the energy levels in the members of any one sub-group showed variations corresponding to the law of the sub-groups connecting the interatomic distances, this law being of the form $\dfrac{d}{n} = \left(\dfrac{1}{aZ}\right)^x$, where x is approximately 1/3 for the elements immediately following the inert gases. Since in the members of any one period a term of the type $\dfrac{1}{Z^x}$ for the interatomic distances corresponds to one of the type Z^{2x} for the energy levels, it appeared natural to search for relations involving $Z^{2/3}$ for the members of any one

sub-group, and in this way some interesting relations have been traced.

The first of these relations may be summarized by saying that for the rare gases and the elements immediately following them if Z is the atomic number, V the ionization potential * necessary to remove an electron of principal quantum number n, then for corresponding valency electrons in the members of any one sub-group n^2V varies linearly with $Z^{2\cdot3}$, and to a first approximation is often directly proportional to $Z^{2\cdot3}$. This relation requires a straight line to be formed when n^2V is plotted against $Z^{2\cdot3}$, and some examples of this are shown in fig. 8.

In this table Z is the atomic number and V the ionization potential necessary for the removal of an electron of quantum number n. The values of V are those calculated from spectral data, and all are from the International Critical Tables, vol. vi. p. 70, except those marked †, which are from Abbink and Dorgelo (*Z. Phys.* 1928, xlvii. p. 221).

The straight line marked I refers to the *first ionization potential* of the alkali metals, and it will be seen that a very good straight line is formed by plotting n^2V against $Z^{2/3}$. Since the first ionization potential of the alkali group refers to the removal of the valency or series electron, the quantum numbers involved are naturally 2 for lithium, 3 for sodium. . . . . The straight line marked II refers to the *first ionization potentials* of the alkaline earths, and it will be seen that a very good straight line is again found by plotting n^2V against $Z^{2/3}$. The line marked III is for the *second ionization potentials* of the alkaline earths (*i. e.*, the work required to expel the second valency electron from an atom which has already lost one of its valency electrons), and it will be seen that a very fair straight line is again obtained.

In Group III. A the matter is complicated by the fact that the three valency electrons are in two sub-groups containing two electrons and one electron respectively. Data have been found in the literature for the potentials corresponding to the removal of the 2_1, 3_1, and 4_1 electrons from boron, aluminium, and scandium respectively, and these three points give a straight line when n^2V is plotted

* The $\frac{\nu}{R}$ values referred to in the preceding section may be converted into the corresponding potentials by multiplying by 13·54.

Fig. 8.
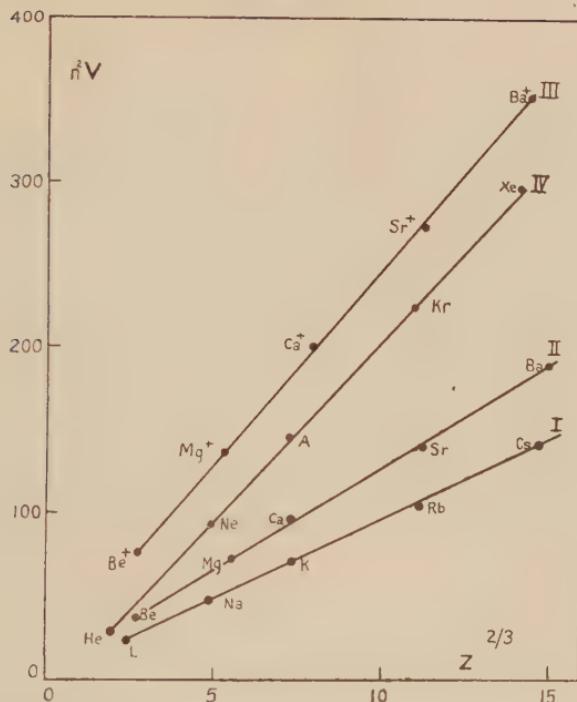
In this figure n^2V is plotted against $Z^{2/3}$, where V is the ionization
potential necessary to remove an electron of quantum number n.
The curves marked I and II refer to the first ionization potentials
of the alkali and alkaline earth sub-group, whilst curve III refers
to the second ionization potential of the alkaline earth group, and
curve IV to the first ionization potential of the rare gas group.
The data are given in Table IV.

TABLE IV.

Element.	Z.	$Z^{2/3}$.	n.	$n^2 V$.	Remarks.	
Li	3	2·08	2	21·4	1st ionization potential.	
Na	11	4·95	3	46	,,	,,
K	19	7·12	4	69	,,	,,
Rb	37	11·1	5	104	,,	,,
Cs	55	14·46	6	140	,,	,,
Be	4	2·52	2	38 and 73·6	1st and 2nd ionization potentials.	
Mg......	12	5·24	3	68·5, 134·5	,,	,,
Ca	20	7·37	4	97·4, 189	,,	,,
Sr	38	11·31	5	141·8, 274	,,	,,
Ba	56	14·63	6	186·7, 358	,,	,,
He	2	1·587	1	24·48	I_I	
Ne	10	4·64	2	85·8, 86·4	L_{III}, L_{II}	
A	18	6·87	3	141, 143	M_{III}, M_{II}	
Kr	36	13·9	4	222†		
Xe	54	14·29	5	300 †		

against $Z^{2/3}$, but it has not been found possible to find data for yttrium.

Finally, the straight line marked IV is that obtained for the first ionization potentials of the inert gases, and it will be seen that a surprisingly good straight line is formed by plotting n^2V against $Z^{2/3}$ for the whole of the five members of this group, and, further, this line passes very nearly through the corresponding point for hydrogen. In the inert gas group the first ionization potentials refer to the removal of the 1_1 electron from helium, but to that of the 2_2, 3_2, 4_2, etc. electrons of the later members, and the author has not yet succeeded in finding data to investigate whether a similar relation holds for the potentials corresponding to the removal of the 1_1, 2_1, 3_1, etc. electrons, but it is clear that the point for helium lies on the straight line formed by the points for the 2_2, 3_2, etc. electrons of the later members.

The above figures, and the straight lines given in fig. 8, refer to the *valency electrons*, and consequently it is only in the inert gas group that these relations can be considered as analogous to those found for the interatomic distances, since in the Law of the Sub-Groups $\dfrac{d}{n} = \left(\dfrac{1}{aZ}\right)^2$ the quantum number n refers to the outermost shell of electrons in the atomic core or ion, and not to the valency electrons, except in the inert gas group, where the two are identical. Unfortunately the available data do not seem sufficiently accurate to enable a critical test to be made as to whether a similar relation holds for the potentials corresponding to the removal of the electrons in the outermost shell of the ion or atomic core, since the values for the N_{II}, O_1, and O_{II} electrons are very uncertain. An approximate straight line is formed by plotting n^2V against $Z^{2/3}$ for the potentials corresponding to the removal of the K_1 electron from beryllium, the L_1 from magnesium, and so on up to the O_I electron from barium, but the agreement is by no means exact, and for the corresponding electrons of the alkali group the linear relation holds less accurately if the figure for the O_I level in cæsium is correct. On the other hand a very good linear relation holds between $Z^{2/3}$ and n^2V for the potentials corresponding to the removal of the K_I, L_{II}, N_{II}, and O_{II} electrons from lithium, sodium, rubidium, and cæsium on the one hand, and from beryllium, magnesium, strontium, and barium on the

other, although wide deviations are in this case shown by
the points for potassium and calcium. It may be signifi-
cant that a wide divergence exists between the published
value for the M_{II} level in potassium as determined by
ionization methods and that determined from spectro-
scopic data. The former value would in fact fit well
on to the line given by plotting n^2V against $Z^{2\cdot3}$ for the
other members of this group, but it does not appear
justifiable to select results in this way, and until accurate
data are available for the N_{II}, O_I, and O_{II} levels it seems
inadvisable to attempt a detailed discussion.

The interesting point to note is that in the inert gas
group the first ionization potentials show a linear relation
between n^2V and $Z^{2/3}$, in which the power of Z is minus
twice that found for the interatomic distances. Further,
exactly similar relations appear to hold for the ionization
potentials of the valency electrons in the alkali and
alkaline earth groups.

VI The Interatomic Distances in the Metals with Hexagonal Close-packed Structures.

In the author's previous paper it was pointed out that
in some of the metals with hexagonal close-packed
structures the axial ratio does not correspond exactly
to that required by close-packed spheres, so that there
are two close distances of approach, and in such cases
the distance which was considered was that given by the
value of a in the close-packed structure. In the case of
close-packed spheres the axial ratio $c/a = 1\cdot63$, and the
second distance of approach is also equal to a, but in some
metals $\dfrac{c}{a} = 1\cdot59$ or $1\cdot62$, and here the second distance of
approach is about 1–2 per cent. less than a. This at
first sight rather arbitrary selection of the value of a as
that to be dealt with was based upon the fact that in the
case of cobalt, which crystallizes both in the face-centred
cubic and the hexagonal close-packed structures, it was
the value of a in the hexagonal form $(c/a = 1\cdot59)$ which
was equal to the interatomic distance in the face-centred
cube. It was further quite undoubted that it was the
value of a which gave the better agreement with the
straight lines required by the Law of the Sub-Groups.
The metals which are affected in this way are beryllium,

magnesium, titanium, zirconium, ruthenium, osmium, and β cobalt, and in view of the complex results described above for the case of manganese it may perhaps be objected that this procedure is unjustified, and that the two distances of approach in β cobalt are due to atoms in two distinct states. It will be appreciated that with the very small differences with which we are concerned in figs. 6 and 7 this point is of importance, since the almost exact confirmation obtained for the predicted values of the manganese atoms in different states depends upon our including the a value (2·95 Å) for titanium, and not the closest distance of approach or the minor axis of the oblate spheroid (2·90 Å). Further, if the two distances of approach in titanium really indicated atoms in different states, the general scheme outlined in Section III. would clearly require modification. It must be admitted frankly that an absolutely conclusive decision does not yet seem possible, but the following points may be regarded as confirming the point of view adopted previously :—

(1) In the cases of carbon and silicon it seems almost certain that the atoms are 4-valent in the solid, and titanium shows very much the same general sequence of interatomic distances and melting-points as compared with potassium and calcium, and agrees well with the Law of the Sub-Groups.

(2) Titanium shows a very small electrical conductivity per atom *, and its negative temperature coefficient of resistance at low temperatures is clearly analogous to the negative coefficient of silicon.

(3) The same axial ratio of 1·59 is shown by beryllium, in which it can hardly be disputed that we are dealing with a simple divalent metal. There is also a distinct difference between cases such as those of manganese, where different types of atoms can be recognized in the structure, and those of the close-packed hexagonal type, in which all the atoms can be represented by oblate spheroids.

The evidence therefore appears very considerable that titanium is 4-valent in the solid, and that the difference

* See the curves given by Bridgman in the Report of the Solvay Congress for 1924.

of the axial ratio from that required by spheres is of the same nature as that found in beryllium ($c/a = 1 \cdot 59$) and magnesium ($c/a = 1 \cdot 62$), and presumably due to some kind of polarization effect. It cannot be disputed that the selection of the a value for theoretical consideration is to some extent arbitrary, but the case of cobalt supplies the necessary justification. This point is dealt with at some length in the hope that an obvious criticism will be met.

VII. Discussion.

In the preceding sections we have presented the relations which have been traced between the interatomic distances and the energy level values in a purely empirical way, and their theoretical interpretation is still obscure.

In the Law of the Sub-Groups, $\dfrac{d}{n} = \left(\dfrac{1}{a\mathrm{Z}} \right)'$, the quantum number n which is involved is that of the outermost shell of electrons in the atomic core or ion, and the first and most obvious interpretation is that it is this shell of electrons which is directly responsible for the size of the atom in the crystal of the element. This conception might be regarded as supported by the results of the present investigation, which show that the relations for the interatomic distances in the elements of any one Period are duplicated by relations for the energy levels of the electrons of the outermost shell of the atomic cores or ions. From this point of view, to use a very crude method of expression, we should regard the outermost shell of electrons as determining the size of the atoms, which would be drawn together by the valency electrons until the outermost shells of electrons in the ions were " in contact." There are, however, very great difficulties in accepting such a simple explanation. The first of these is the fact that the interatomic distances increase on passing from the inert gases to the following alkali metals, in spite of the fact that the low melting-points of the inert gases indicate a much weaker type of binding. Thus for argon $d = 3 \cdot 84$ Å. whilst for potassium $d = 4 \cdot 37$ Å, so that there is an increase of more than $0 \cdot 5$ Å, although it seems almost inevitable that the size of the M shell of electrons is greater in argon than in potassium, and it is well known that the repulsion falls off as an inverse high power

of the distance. As was pointed out in the previous paper, it is clear that this increase is due to the mutual repulsion of the potassium ions in the metal, but in this case it is difficult to see why the interatomic distances should be so simply related to the quantum numbers or energy levels of the M electrons, since we should expect the major part of the repulsion to be due to the simple electrostatic repulsion of the ions, and the direct forces between the M shells to appear only as a small correction factor. Another difficulty is that it is the M_{III} and M_{II} electrons rather than the M_I electrons which would be expected to exert the chief effect from the above simple point of view, whereas the correspondence traced refers to the M_1 electrons. Further, the electron distributions calculated by Hartree[7] and others for these atoms indicate that the M shells in atoms of potassium, the N shells in atoms of rubidium, etc. are very much smaller than the atomic radii of the atoms in the metallic crystal, so that the mutual effect of the M shells of two neighbouring atoms should be extremely small at the distances of approach in the crystal of the metal. It may of course be suggested that it is just this small residual effect which distinguishes one metal from another, and prevents all the univalent metals from having the same interatomic distances, but a more probable explanation would appear to be that the attractions of the valency electrons are not the same in the different Periods, and that the difference is due principally to the effect of the outermost shell of electrons of the atomic core or ion. That is to say, whilst the valency electrons are attracted by, or shared between, the atoms in the crystal, and so serve to bind them together, this attraction for the atom as a whole is accompanied by a repulsion for the outermost shell of electrons in the atomic core or ion, so that the latter exerts an indirect effect upon the net attractive force, and hence upon the interatomic distance. But why this indirect effect should correspond to such simple relations between the interatomic distances and the quantum numbers and energy level terms is at present quite unknown, although the straight lines in the logarithmic diagrams suggest clearly that for some properties the structures of complex atoms can be treated as though successive electrons cut off definite fractions of the nuclear charge.

It must be admitted frankly that the relations which have been described in the present paper are purely empirical, and the conclusions which have been drawn must to some extent be looked upon as tentative, and without any really sound theoretical basis. But, whatever may be its meaning, the correspondence between the interatomic distances and the energy level terms appears to be so general in the first four Periods, that it seems probable that the conclusions which have been drawn as to the states of the atoms have considerable justification and can hardly be wrong by more than one electron per atom. Even when the utmost possible allowance is made for points such as those described in the preceding section, the conclusion appears almost inevitable that the relations between $\log \dfrac{\nu}{R}$ and $\log Z$ correspond to those between $\log d$ and $\log Z$, provided that the scale for $\log \dfrac{\nu}{R}$ is made minus one half that for $\log d$, and such a general correspondence can hardly be considered as a mere coincidence.

VIII. Acknowledgements.

Summary.

1. If Z is the Atomic Number the interatomic distances in the crystals of the elements vary as $\dfrac{1}{Z}$, $\dfrac{1}{Z^2}$, $\dfrac{1}{Z^3}$, and $\dfrac{1}{Z^5}$ for the elements at the beginning of the first, second, third, and fourth Periods respectively. At the same time the electronic energy levels vary linearly with Z^2, Z^4, Z^6, and Z^{10} for the N_1 electrons of the outermost group of electrons of the atomic core or ion (*i. e.* the 2_1 electrons for Sodium, Magnesium, etc., the 3_1 electrons for Potassium,

Calcium, etc.), and this linear relation is often a direct proportionality.

2. This empirical correspondence, whereby a variation of the interatomic distance as $\dfrac{1}{Z^x}$ accompanies a variation of the electronic energy level terms as Z^{2x}, has been used for a detailed discussion of the interatomic distances in the crystals of the transitional elements of the Long Periods, and a method is suggested for determining the electronic states of the atoms in the solid crystals, as distinct from those in the free vapour. The main con-conclusion is that in the solid crystals the transition process only begins at Group VI., whereas in the case of free atoms it begins at Group III.

3. For the valency electrons it is shown that in Groups O, I. A, and II. A, if V is the ionization potential, a linear relation exists between n^2V and $Z^{2.3}$ for the members of any one group where n is the quantum number of the electron.

4. Recent data show that in Group O (the Rare Gases) the interatomic distances (d), agree with the Law of the Sub-Groups, $\dfrac{d}{n} = \left(\dfrac{1}{aZ}\right)^x$, where n is the principal quantum number of the outermost shell of electrons of the atomic core, which in this group is the outermost shell in the atom. The value of x is very nearly $\frac{1}{3}$ as in Groups I. A, II. A, and IV. A.

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The Old Chemistry Department,
    The University Museum, Oxford.
        November 1930.

LVI. *Excitation of the Visible Spectrum of Helium. By*
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1. IN order to form a theory to explain the uniform
positive column in direct current discharges or the
luminous columns in oscillatory discharges it has been
found necessary to attribute the ionization of the gas
and the light from the discharge to direct effects of
collisions of electrons with molecules of the gas.

This theory, which was given many years ago †, is in
general agreement with the properties of the long luminous
discharges in monatomic gases ‡, but it is of interest
to extend these investigations and to find more precisely
the connexion between the intensity of the light emitted
by the gas and the energies of the electrons.

With monatomic gases in tubes about 3 cm. in
diameter the intensity of the light in the visible spectrum
due to a given current is small when the pressure is
large (about 20 or 30 mm.), but the intensity increases as
the pressure is reduced.

A large increase in the light is thus obtained when the
pressure is reduced from about 10 mm. to 2 mm., although
the increase in the mean energy of agitation of the
electrons is comparatively small.

2. The energies of the electrons are distributed about the
mean energy E_1, and a small proportion of the total
number of electrons in the gas have energies E_x which
are much greater than the mean energy E_1. When
electrons with the large energies E_x collide with atoms of
the gas some of the atoms acquire energy from the elec-
trons in amounts which are sufficient to excite radiation.
The large increase in the intensity of the light emitted by
the gas due to a small increase in the mean energy of
agitation E_1 is accounted for by the theory of the dis-
tribution of the energies, which shows that there is a large
increase in the number of electrons with the large energies

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* Communicated by the Authors.
† 'Electricity in Gases,' Sections 274 and 302.
‡ Phil. Mag. ix. (June 1930).

E_x corresponding to a small increase in the mean energy E_1.

It has been found from considerations of the electrical properties of the currents that the electrons do not recombine with positive ions in the gas to any appreciable extent, so that the light from the discharge cannot be attributed to recombination.

3. The theory may be used to find approximately the energies E_x of the electrons which excite the radiation in different parts of the spectrum.

The mean energy of agitation E_1 has been found in terms of the ratio X/p by experiments on the lateral diffusion of a stream of electrons moving under an electric force X through a gas at pressure p.

The mean energy E_1 of the electrons in the uniform luminous column of a discharge may thus be obtained from the electric force X in the direction of the axis of the tube and the pressure p. In the uniform discharges the force is independent of the current, but it changes with the pressure. For a large range of pressures the force diminishes, but the ratio X/p increases as the pressure is reduced. Thus the energy E_1 is independent of the current, and E_1 increases with the ratio X/p when the pressure is reduced. Also the number of electrons with energies E_r between any given limits is proportional to the current.

In order to find the energies E_r of the electrons in the collisions which cause the atoms to emit rays in different parts of the spectrum it is necessary to find the changes in the intensity of the light due to changes in the mean energy E_1 of the electrons. The effect of changing the mean energy may be deduced from observations of the changes in the intensity of the light due to changes in the pressure of the gas. The following experiments have therefore been made with helium over a range of pressure from 20 mm. to 2 mm.

4. The arrangment of the apparatus is shown in the figure. The gas was contained in a pyrex tube which had two internal electrodes, A and B. The connexion to the electrode A was made through a flexible strip of aluminium foil, and a piece of soft iron was attached to the electrode. It was thus possible to change the distance between the two electrodes by moving A with a magnet.

The precautions adopted to obtain pure gas were the same as those described in previous papers. With a direct-vision spectroscope no lines due to impurities were observed in the light from the discharge.

A direct current discharge was maintained in the gas by connecting the electrodes to a direct-current generator through a two-electrode valve, and the current was adjusted to any required value by regulating the temperature of the filament of the valve.

The light from the uniform column of the discharge fell on a selenium cell S, which was screened from the light of the room. The light passed through a colour filter F, which limited the light falling on the selenium to a definite range of wave-lengths in the visible spectrum. The selenium cell was connected in an arm of a Wheatstone bridge in order to measure the effect of the light on the resistance. The resistance depends on the potential
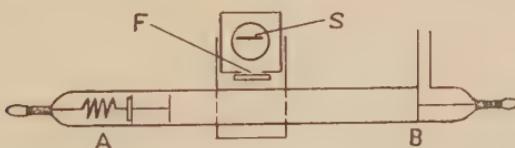

Diagram of apparatus.

between the terminals of the cell and on the time of exposure of the selenium to the light from the discharge tube. It was found that the best method of investigating the effects of changes of pressure was to adjust the current through the gas so as to have the same intensity of light falling on the selenium in the experiments at different pressures.

At the higher pressures much larger currents are required than at the lower pressures. Thus, when the light from the discharge was passed through a red filter it was found that a current of 1·5 milliamp. with the helium at 2·3 mm. pressure gave the same effect on the selenium as a current of 4 milliamp. with the helium at 10·4 mm. pressure.

When the light passed through a violet filter a current of ·92 milliamp. with the helium at 2·3 mm. pressure gave the same effect as a current of 4 milliamp. with 10·4 mm. pressure. Hence, if the same current were

maintained at the different pressures the red light would
be increased in the proportion of $2 \cdot 7 : 1$ and the violet
light in the proportion $4 \cdot 3 : 1$ when the pressure of the
helium is reduced from $10 \cdot 4$ mm. to $2 \cdot 3$ mm.

5. The mean velocities W of the electrons in the direction
of the electric force and the mean energies of agitation E
have been obtained in terms of the ratio Z/p, and the
following are the values of W and E in these experiments.
With the gas at $2 \cdot 3$ mm. pressure the force in the uni-
form column was $6 \cdot 9$ volts per cm., so that $Z/p = 3$. and
the corresponding values of W and E are $W = 1 \cdot 75 \times$
10^6 cm. per sec. and $E = 5 \cdot 2$ volts.   With the gas at
$10 \cdot 4$ mm. pressure the force is $19 \cdot 5$ volts per cm.,
$Z/p = 1 \cdot 9$, $W = 1 \cdot 2 \times 10^6$ cm. per sec., and $E = 3 \cdot 7$ volts.
The energies of the electrons are not all the same in
the collisions which cause the atoms to emit light of a
definite wave-length, so that it is necessary to consider
the mean energy of the electrons in these collisions.   Thus
E_x may be taken to represent the mean energy of the
electrons in the collisions which cause atoms to emit
light within a certain range of wave-lengths.   In the
cases which are here considered, where the mean energy
of all the electrons is about 4 volts. the energy E_x required
to excite radiation is large compared with the mean energy,
and the number of electrons N_x which have energies
exceeding E_x is comparatively small.

In the steady state of motion in a uniform field of force
the energy acquired by the electrons by moving in the
direction of the electric force is equal to the energy lost
in collisions with atoms of the gas.   In general when
E is small the mean loss of energy of electrons in col-
lisions is $\lambda \dot{E}$, where λ is constant over a large range of
values of E in monatomic gases. and is equal to $2 \cdot 5 \times 10^{-4}$
in helium * ;   but. in addition to these losses in small
amounts, the electrons moving with the larger energies
E_x lose a large part of their energies in some of the collisions
with atoms of the gas.   The experiments on the motion
of electrons show that the total loss of energy of the
electrons is principally due to the losses in small amounts
when the mean energy of agitation is less than 4 volts.

* 'Motion of Electrons in Gases,' Clarendon Press.

6. Under these conditions the distribution of the energy of the electrons about the mean energy may be found from the results of the experiments on the diffusion of electrons moving in a uniform field of force *.

An expression of the form $N_x/N = \phi(E_x/E_1)$ is thus obtained for the number N_x with energies exceeding E_x in terms of the total number of electrons N and the mean energy of agitation E_1.

It will be assumed that the distribution of the energies about the mean energy in these experiments is given by the above formula, although in the experiments with the gas at 2·3 mm. pressure (where the ratio $Z/p=3$) the losses of energy in large amounts have an appreciable effect in reducing the mean energy of the electrons. This point will be examined more closely in another set of experiments which are being made to compare the changes in the intensity of the light in the ultra-violet spectrum with the changes in the visible spectrum. Also it may be assumed that the change in the mean energy E_x of the electrons which excite radiation within a certain range of wave-lengths is comparatively small when the mean energy of agitation is changed from E_1 to E_2 by changing the pressure of the gas. In fact, for a first approximation it is assumed that the increase in the intensity of the light due to a given current is proportional to the increase in the number of collisions in which the energies of the electrons exceed a certain value E_x.

7. Let W_1 be the mean velocity in the direction of the electric force, E_1 the mean energy of agitation, and N_1 the number of electrons in the space between two planes perpendicular to the axis of the tube and at 1 cm. apart when the gas is at the pressure p_1 (2·3 mm.) and a given current flows through the tube ; and let W_2 be the mean velocity, E_2 the mean energy, N_2 the number between the two planes when the pressure is p_2 (10·4 mm.) and the same current flows through the tube. Since the current is the same at the two pressures, N_1W_1 is equal to N_2W_2. The number of electrons in the space between the two planes with energies exceeding E_x is $N_1\phi(E_x/E_1)$ when the gas is at the pressure p_1, and the number of collisions C_1 between these electrons and atoms of the gas is proportional to $N_1p_1\phi(E_x/E_1)$. Similarly the number of

* Phil. Mag. ix. p. 1145 (June 1930).

collisions C_2 in the same space between the electrons with energies exceeding E_x and the atoms of the gas is proportional to $N_2 p_2 \phi(E_x/E_2)$ when the gas is at the pressure p_2. The following expression is thus obtained for the ratio C_1/C_2 :—

$$\frac{C_1}{C_2} = \frac{N_1 p_1 \phi(E_x/E_1)}{N_2 p_2 \phi(E_x/E_2)} = \frac{W_2 p_1 \phi(E_x/E_1)}{W_1 p_2 \phi(E_x/E_2)}.$$

Since the intensity of the light of a given wave-length is proportional to the number of collisions in which the energy of the electrons exceeds a given amount, the ratio C_1/C_2 is the ratio of the intensities of the light obtained experimentally. Thus, if E_r be the mean energy of the electrons which excite the light that traverses the red filter, and C_1 and C_2 the intensities of this light due to a given current at the pressures $p_1 = 2\cdot3$ mm. and $p_2 = 10\cdot4$ mm., the ratio C_1/C_2 is $2\cdot7 : 1$, and the following equation is obtained to determine E_r :

$$\phi(E_r/5\cdot2) = 18\phi(E^r/3\cdot7),$$

since the mean energies of the electrons at these pressures are $5\cdot2$ volts and $3\cdot7$ volts respectively.

Similarly, if E_v be the mean energy of the electrons in the collisions which excite the light that traverses the violet filter, the ratio C_1/C_2 is $4\cdot3 : 1$, and the equation to determine E_v becomes

$$\phi(E_v/5\cdot2) = 28\phi(E_v/3\cdot7).$$

The values of $\phi(E_x/E_1)$ are given for several values of (E_x/E_1) from $1\cdot5$ to $4\cdot5$ in the paper on the energies of electrons in gases *.

The number $\phi(E_x/E_1)$ diminishes as (E_x/E_1) increases, and the value of $E_r/5\cdot2$ is obtained from the condition that $\phi(E_r/E_1)$ is reduced in the proportion $1 : 18$ by increasing E_r/E_1 in the proportion $5\cdot2 : 3\cdot7$, that is $1\cdot4 : 1$. This condition is satisfied at the point $(E_r/E_1) = 2$, since $\phi(2) = \cdot052$ and $\phi(2\cdot8) = \cdot003$. Thus $E/5\cdot2 = 2$, so that the potential $E_r = 10\cdot4$ volts.

Similarly it is found that the potential $E_v = 11\cdot1$ volts.

8. The figures show that although the intensity of the red light due to a given current is increased in the proportion $2\cdot7 : 1$ when the pressure of the gas is reduced

from 10·4 to 2·3 mm. and the violet light in the proportion 4·3 : 1, the difference between the mean energies of the electrons which excite the light at the red and violet ends of the spectrum is comparatively small.

The red filter used in these experiments was one of a set of spectrum filters made by Messrs. Ilford. The filter was cemented between two squares of plate glass, and it transmitted light of wave-lengths between 6200 Å. and the red end of the visible spectrum. The violet filter was of a similar type and transmitted light of wavelengths in the range from 3900 Å. to 4850 Å. Experiments were also made with the light that passed through yellow and green filters, and the changes in the intensity due to changes of pressure were found to be between those obtained with the red and violet filters.

The values of E_r and E_v given above are the mean energies of the electrons in the collisions with atoms of the gas which excite red and violet light. They do not represent the loss of energy in these collisions.

The experiments, where the mean energies of the electrons are about 3 or 4 volts, therefore show that it cannot be supposed that large energies of amounts from 20 to 24 volts must be acquired by the atoms of helium before the lines of the visible spectrum are emitted.

The results of the experiments are therefore not in agreement with the properties of the Bohr model of the helium atom, which requires energies exceeding 20 volts before it gives out any radiation.

LVII. *Some Remarks on the Paper of S. Chandrasekhar " The Ionization-Formula and the New Statistics "* *. *By* WILHELM ANDERSON, *Dr. phil. nat. (Tartu-Dorpat)* †.

S. CHANDRASEKHAR ignores the variability of the mass of the electron, which with temperatures above 10^9 degrees must lead to considerable errors.

In my paper " Über die ' mechanische ' Ionisation von Gasen durch extremen Druck bei beliebig tiefer Temperatur " I have shown that with increasing pressure

the ionization potential must diminish and in the end become equal to zero [*]. Thus, *e. g.*, in the case of hydrogen the ionization potential vanishes at a pressure of $3 \cdot 5 \times 10^{12}$ dyn. cm [2]. Chandrasekhar says : '' Thus the para-doxical statement results that the electrons, though all of them bound, are free '' [†]. This is in agreement with my words : '' Ein solches Gas . . . kann mit gleichem Rechte als ionisiert wie als unionisiert angesehen werden '' [‡].

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LVIII. *The Surface Tensions of Aqueous Solutions of p-Toluidine. By* R. C. BROWN. *B.Sc., Lecturer in Physics, University College, London* [§].

A PAPER by Gans and Harkins [‖] has recently appeared drawing attention to the fact that there is appa-rently no very definite information with regard to the relation between surface tension and concentration of solutions of p-toluidine in water. These authors have therefore determined the relation. using the drop-weight method. In reviewing the published results of other experimenters they point out that the curve obtained by Frumkin, Donde and Kulvarskaya [¶]. using the method of capillary rise, whilst agreeing with their own drop-weight method results, is widely different from that obtained by Edwards [**], who used Ferguson's modification [††] of the capillary rise method. In his paper Edwards remarks hat a few points determined by the use of the ring method as embodied in the du Noüy tensiometer did not lie on his curve. In a private communication the attention of Dr. Ferguson was drawn to this, and it was suggested that the present author should determine the curve by

[*] W. Anderson, *Phys. Zeitschr.* xxx. p. 360 (1929).
[†] S. Chandrasekhar, *l. c.* p. 299.
[‡] W. Anderson, *l. c.* p. 362.
[§] Communicated by Prof. E. N. da C. Andrade, D.Sc.
[‖] Journ. Amer. Chem. Soc. lii. p. 2289 (1930).
[¶] *Zeit. für physik. Chem.* cxxiii. p. 321 (1926).
[**] Journ. Chem. Soc. cxxvii. p. 744 (1925).
[††] Trans. Farad. Soc. xvii. pt. 1, p. 384 (1921).

several different methods, in order to make certain whether
the discrepancy was real.

This work was carried out at East London College
some time ago, but was not published. Now that the
subject has been reopened, however, it may be of interest
to record the results.

Methods Used.

Ring Method.

The ring was made of platinum wire and was of approxi-
mately the same dimensions as that supplied with the du
Noüy tensiometer, namely, mean radius of ring 0·687 cm.,
mean radius of wire 0·016 cm. It was suspended from the
underside of a light pan attached to the arm of a torsion
balance, the head of which was not graduated but could be
rotated by a slow-motion device. After the ring had been
pulled off the surface of the solution by twisting the torsion
head, by putting weights in the pan the torsion arm was
brought back to the position which it occupied when the
rupture of the surface took place.

The method is simple, and the readings were consistent.
The chief objection to the ring method is the uncertainty
of the expression for the value of the maximum pull which
is measured by the apparatus. It would seem, however,
that the simple formula, viz., twice the average circum-
ference of the ring multiplied by the surface tension, is
not very far from the truth *.

Rectangular Frame.

With most of the solutions it was possible to form a
stable film in a rectangular frame made from thin glass
tubing. The pull on the frame due to the film was
measured by means of the torsion balance and the surface

* For a description of the du Noüy tensiometer see du Noüy, Journ.
Gen. Physiology, i. p. 521 (1919), and for mathematical theories of
the ring method see Cantor, *Ann. der Phys.* xlvii. p. 399 (1892),
MacDougall, 'Science,' lxii. p. 290 (1925), and Freud & Freud, Journ.
Amer. Chem. Soc. lii. p. 1772 (1930). Since the completion of this
research, tables of corrections to the ring method (compiled from experi-
mental data) have been published by Harkins and Jordan (Journ. Amer.
Chem. Soc. lii. p. 1751 (1930). When these corrections are applied to
the ring-method results in the present paper, the following values are
obtained for surface tensions corresponding to concentrations of 0·0,
0·1, ... 0·6 gm./100 c.c.—72·2, 68·0, 62·3, 57·7, 53·7, 50·6, 48·2. It
will be seen that these agree much less with the values obtained by other
methods than do the uncorrected figures.

tensions were calculated by means of the usual simple formula *.

Ferguson's Method.

The technique employed followed closely that described by Ferguson. The pressure necessary to force the liquid meniscus down to the end of the thick-walled capillary tube standing vertically in the solution was measured with an aniline manometer. If, after this measurement has been taken, the pressure necessary to detach a bubble from the capillary tube is observed, the method becomes that known as Jaeger's method, and the control of the rate of production of bubbles is more precise than if the usual practice is adopted, namely, that of allowing a slow continuous current of air to enter the space above the meniscus.

Capillary Rise.

For this method a piece of thick-walled glass capillary of uniform bore was chosen. This was cleaned by boiling it in chromic acid before each measurement of surface tension was made, and washing it with water and then with the solution under test. It was set vertically in the solution to such a depth that the meniscus stood at the level of a file mark on the tube. The height of the bottom of the meniscus above the general level of the liquid was measured by setting a steel needle of known length vertically with its point just touching the plane surface of the liquid, and, by means of a cathetometer, observing the difference between the levels of the top of the needle and the bottom of the meniscus. When all the solutions had been measured the tube was broken at the file mark and its mean radius measured.

Pull on a Sphere.

The surface tensions of two or three solutions were determined by measuring the vertical pull exerted on a hollow glass sphere when its lowest point was in the general level of the free surface of the liquid †.

Solutions were prepared by dissolving a known weight of solid p-toluidine in distilled water and making the

* For discussions of the plane film method see Proctor Hall, Phil. Mag. xxxvi. p. 385 (1893), and Lenard, Dallwitz - Wegener, and Zachmann, *Ann. der Phys.* lxxiv. p. 381 (1924).
† Ferguson, Phil. Mag. xxvi. p. 925 (1913).

volume up to 250 c.c. ; all concentrations were expressed in gm. per 100 c.c. of solution. A fresh solution was made for each determination. No very special precautions were taken with regard to the constancy of the temperature. The mean temperature of the solutions was 16·6°C., and the accuracy of all the surface-tension measurements probably about 0·5 per cent. The p-toluidine used in all measurements was recrystallized from petroleum ether.

Results.

The results obtained by all methods were in fairly close agreement with those obtained by Gans and Harkins. The values given by Ferguson's method in no way followed those published by Edwards using the same method ; they were much nearer to his isolated points given by the ring method and to all curves determined by the present author. The ring and frame methods were used on the same solutions, and almost identical curves resulted *. Ferguson's method gave a curve which was somewhat steeper at the point of inflexion than the other curves.

For purposes of comparison the following table has been prepared, all the figures having been read off from curves.

Surface tensions of aqueous solutions of p-toluidine in dynes/cm.

c. gm./100 c.c. of solution.	Edwards. (Ferguson's method.)	Brown.				Gans & Harkins (drop-weight).
		Ferguson's method.	Ring.	Capillary rise.	Mean.	
0·0	74·9	73·2	74·0	72·7	73·3	72·7
0·1	69·6	71·8	70·0	71·7	71·2	70·6
0·2	59·9	66·1	64·8	66·0	65·6	65·1
0·3	54·1	59·5	60·3	61·3	60·4	60·2
0·4	49·4	55·8	56·5	57·0	56·4	56·5
0·5	45·5	53·1	53·6	54·3	53·7	53·3
0·6	42·4	50·7	51·0	51·9	51·2	50·9
		Average temperature....			16·6° C.	20·0° C.

* The following series of figures emphasises the agreement between the (uncorrected) ring and frame values for the *same* solutions :—

| Ring......... | 63·3 | 59·8 | 53·3 | 51·1 |
| Frame .... | 63·4 | 59·7 | 53·5 | 51·4 |

These figures are interesting in view of the fact that by applying Harkin's and Jordan's corrections to the ring method values, these latter are lowered by anything up to 3 dynes/cm. Either the frame method needs a correction of this magnitude (which seems unlikely) or the tables of Harkins and Jordan are not applicable to these ring method results.

It will be seen that there is a fair agreement between the mean values for the three different methods used by the author and those of Gans and Harkins. It would be expected that the results of Gans and Harkins should be rather lower on account of the difference between the two temperatures, and this is seen to be the case except for one pair of values. Results given by the pull on the sphere were about one dyne per cm. lower than the ring method values. A larger measure of agreement might have been expected between Ferguson's method and capillary rise. Possibly the higher values given by the capillary rise method for the more concentrated solutions are due to adsorption of the p-toluidine on to the wall of the capillary tube and a consequent lowering of the concentration in the meniscus. The possibility of such adsorption is greatly reduced in Ferguson's method. The fact that the values obtained by the two methods which depend on contact angle—namely, capillary rise and Ferguson's method—are near to those given by methods independent of contact angle shows that the angles of contact between the various solutions and glass in air must be sensibly zero.

The author desires to express his thanks to Dr. A. Ferguson for the helpful interest which he has displayed in the work.

LIX. *On Langmuir's Adsorption Isotherm.* *By* R. S. BRADLEY [*].

THE various isotherms proposed from time to time to express the adsorption of a gas by a solid have all been criticized. Freundlich's isotherm

$$x = \alpha p^{\frac{1}{n}},$$

where x is the weight adsorbed per constant area of adsorbent, α is a constant, n a constant, and p the pressure, has no theoretical basis, and x increases indefinitely with p instead of reaching a maximum. Langmuir's equation

$$x = \frac{c_1 c_2 p}{1 + c_2 p},$$

where c_1 and c_2 are constants, has been criticized by Polanyi [1] on the grounds that Langmuir's derivation makes no allowance for the temperature variation of c_1, the adsorption maximum, while he finds that c_2 should vary as $V e^{\frac{E}{KT}}$, where V is the volume of action of one active spot, and E is the adsorption energy. Experimentally both c_1 and c_2 vary with temperature, and c_2 not in the manner calculated by Polanyi. As Wilkins and Ward [2] point out, there will be a slight decrease in c_1 due to the increase in the lattice spacing on increasing the temperature, but this will be much smaller than the observed decrease. There is also the indeterminate possibility of a change in the number of active centres with temperature. Frenkel's [3] adsorption equation, when correctly formulated, as Wilkins and Ward have done, in the form

$$\frac{S}{n} = \sigma_0 \left(1 + \frac{\sqrt{2\pi m KT}}{p\sigma_0\tau_0} \cdot e^{\frac{-u_0}{KT}} \right),$$

also gives an adsorption maximum independent of the temperature, and, in fact, saturation corresponds to a close-packed monomolecular layer. Here n is the number of molecules of area σ_0 and verwelzeit τ_0 adsorbed on area $S : u_0$ is the adsorption energy.

Polanyi's own theory of adsorption is open to criticism, and is not in accord with modern ideas on intermolecular force. As Kruyt and Moddermann [4] have shown, the adsorption potential of Polanyi and the heat of adsorption cannot be identified. We have

$$\epsilon = q + T \cdot \frac{d\epsilon}{dT},$$

where ϵ is the adsorption potential and q is the heat of adsorption. The vanishing of $\frac{d\epsilon}{dT}$ therefore requires that ϵ and q are equal, and that $\frac{dq}{dT}$ is zero. This is not found. Later Goldmann and Polanyi [5] assumed that while the adsorption potential is invariant with the temperature the affinity is not, and changes with the dilatation of the liquid. But the values of the dilatation calculated from the affinity curves do not correspond with the experimental results.

The treatment of adsorption as a case of capillary condensation [6] is inconclusive, as we do not know how the radius of curvature of a microcapillary liquid surface affects the pressure, and, indeed, the use of macroscopic conceptions in

this region is of doubtful significance. Moreover, there are internal inconsistencies, as pointed out by Coolidge [7].

Zeise [8] has shown that Langmuir's equation can be applied to the adsorption of gases on charcoal, and that a good agreement is obtained. There is no need therefore to adopt in this case the method of Polanyi, which gives a poorer agreement. The meaning of the constants in Langmuir's equation is, however, left open. They are found to vary with the absolute temperature according to

$$c_1 = a_1 - b_1 T, \quad \ldots \quad \ldots \quad (1)$$

$$c_2 = \frac{10^{a_2}}{T^{b_2}}, \quad \ldots \quad \ldots \quad (2)$$

where a_1, b_1, a_2, b_2 are constants, giving the empirical adsorption formula, which fits the fact very well,

$$x = \frac{10^{a_2}(a_1 - b_1 T) \cdot T^{-b_2} p}{1 + 10^{a_2} \cdot T^{-b_2} \cdot p} .$$

In this paper the temperature variation of c_1 and c_2 will be determined theoretically, and the results are found to be equivalent to those of Zeise expressed above.

Wilkins and Ward have remarked that the variation of c_1 found by Zeise can be accounted for by supposing that at saturation a constant pressure is exerted by the adsorbed phase, and that the effect of temperature is the same as that on the mass of gas enclosed in a constant volume at constant pressure. But in this case the equation of Zeise is not found, since the relation for a perfect gas is

$$\frac{x}{x_1} = \frac{T_1}{T},$$

where T is the absolute temperature. This is equivalent to

$$x = x_0/(1 + \alpha t) = x_0(1 - \alpha t),$$

where t is the centigrade temperature. Thus $\dfrac{d \log c_1}{dT}$ should be compared, not with $\dfrac{1}{V_0} \dfrac{dv}{dT}$ for a gas, but with $\dfrac{1}{T}$. A relation of the form found by Zeise can be derived if the gas is considered to be imperfect. Thus for an imperfect gas obeying the equation

$$p(V - b) = RT,$$

where V is the volume of 1 gm. mol.,

$$\frac{1}{x} = \frac{b}{V} + \frac{RT}{pV},$$

$$x = \frac{b}{V} - \frac{RT}{pV} = c_1,$$

if $\dfrac{R}{pb}$ is small. We note from Zeise's results that $\dfrac{b_1}{a_1}$ is roughly $2 \cdot 5 \ 10^{-3}$ for the various gases, and as b does not vary greatly we obtain a rough value of p from

$$\frac{b_1}{a_1} = \frac{R}{pb}.$$

This gives p as roughly 50 dynes per cm., which corresponds roughly to a pressure of about 2000 atmospheres.

Langmuir's isotherm may be derived [9] by a thermo-dynamic method. This is now extended to include the temperature variation of c_1 and c_2.

The theory of imperfect gases may be taken over to the two-dimensional phase. Onnes found for a bulk gas that

$$p\mathrm{V} = \mathrm{RT}\left(1 + \frac{\mathrm{B}}{\mathrm{V}} + \frac{\mathrm{C}}{\mathrm{V}^2} + \frac{\mathrm{D}}{\mathrm{V}^4}\cdots\right),$$

where the constants B, C, D vary with temperature according to

$$\mathrm{B} = b_1 + \frac{b_2}{\mathrm{T}} + \frac{b_3}{\mathrm{T}^2} + \ \ldots \ \text{etc.}$$

Simple theory [10] reproduces this equation to the term in $\dfrac{1}{\mathrm{V}}$ in the form

$$p\mathrm{V} = \mathrm{RT}\left(1 + \frac{\mathrm{B}}{\mathrm{V}}\right),$$

where

$$\mathrm{B} = 2\pi \int_0^\infty r^2 \left(1 - e^{\frac{\phi}{\mathrm{KT}}}\right)dr$$

$$= \frac{2\pi}{3\mathrm{KT}}\int_0^\infty r^3 f(r) \ . \ e^{\frac{\phi}{\mathrm{KT}}}dr,$$

where $\phi(r)$ is the potential field of a molecule, and $f(r)$ is the force between two molecules separated by a distance r.

The equation of Beattie and Bridgman [11] has the merit of giving the virial equation in terms of only five constants. The equation runs

$$p = \frac{\mathrm{RT}}{\mathrm{V}^2}(1 - \epsilon)\left[\mathrm{V} - \mathrm{B}\right] - \frac{\mathrm{A}'}{\mathrm{V}^2},$$

where

$$\mathrm{A}' = \mathrm{A}_0\left(1 - \frac{a}{\mathrm{V}}\right), \quad \mathrm{B} = \mathrm{B}_0\left(1 - \frac{b}{\mathrm{V}}\right), \quad \text{and} \quad \epsilon = \frac{\mathrm{C}}{\mathrm{V}\mathrm{T}^3}.$$

In the virial form this becomes

$$p = \frac{\mathrm{RT}}{\mathrm{V}} + \frac{\mathrm{RT}}{\mathrm{V}^2}\left(\mathrm{B}_0 - \frac{\mathrm{C}}{\mathrm{T}^3} - \frac{\mathrm{A}_0}{\mathrm{RT}}\right)$$

$$+ \frac{RT}{V^3}\left(\frac{cB_0}{T^3} - bB_0 + \frac{aA_0}{RT}\right) - \frac{B_0 cb}{V^4 T^3} \cdot RT$$

$$= \frac{RT}{V} + \frac{RT}{V^2}\beta + \frac{RT}{V^3}\gamma + \frac{RT}{V^4}\delta.$$

The free energy takes the form

$$\int V dp = RT\left[-\log V + \frac{2\beta}{V} + \frac{3\gamma}{2V^2} + \frac{4\delta}{3V^3}\right] + F_0,$$

where F_0 is the reference value. This is the form used in this paper, and by analogy the equation for the two-dimensional phase may be written

$$\int A dp = RT\left[-\log A + \frac{2\beta}{A} + \frac{3\gamma}{2A^2} + \frac{4\delta}{3A^3}\right] + F_0,$$

where β, γ, δ vary with temperature as above.

The free energy of the bulk gas is $RT\log p + F_0'$, where p is the pressure. Hence, if x is the number of gm. mols. adsorbed per unit area, $= \frac{1}{A}$,

$$\log p + \frac{F_0'}{RT} = \log x + 2\beta x + \frac{3}{2}\gamma x^2 + \frac{4}{3}\delta x^3 + \frac{F_0}{RT}.$$

This is the adsorption isotherm, and it remains to link it with Langmuir's equation. The latter may be written

$$p = \frac{x}{c_1 c_2 - c_2 x},$$

or

$$\log p = \log x - \log(c_1 c_2 - c_2 x)$$

$$= \log x - \log c_1 c_2 - \log\left(1 - \frac{x}{c_1}\right)$$

$$= \log x - \log c_1 c_2 + \frac{x}{c_1} + \frac{x^2}{2c_1^2} + \ldots,$$

since x is always less than c_1.

This is, indeed, the theoretical form provided

$$\frac{1}{c_1} = 2\beta = 2\left(B_0 - \frac{c}{T^3} - \frac{A_0}{RT}\right), \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

$$\frac{\Delta F_0}{RT} = -\log c_1 c_2. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

Equation (3) is, in fact, obeyed, except at high temperatures. If we select the case of CO_2, for which there are most points,

we find that the variation of c_1 with T can be expressed equally well by the equation

$$\frac{1}{c_1} = -\cdot509 + \frac{15\cdot9}{T} + \frac{310^5}{T^3}$$

as by equation (1) above, except for one point. If $\frac{10^3}{c_1} - \frac{310^8}{T^3}$ is plotted against $\frac{10^3}{T}$, a straight line is obtained (fig. 1). For practical convenience equation (1) above is preferable, but the molecular constants of the virial equation cannot readily be derived from it : and, as Wilkins and Ward

Fig. 1.
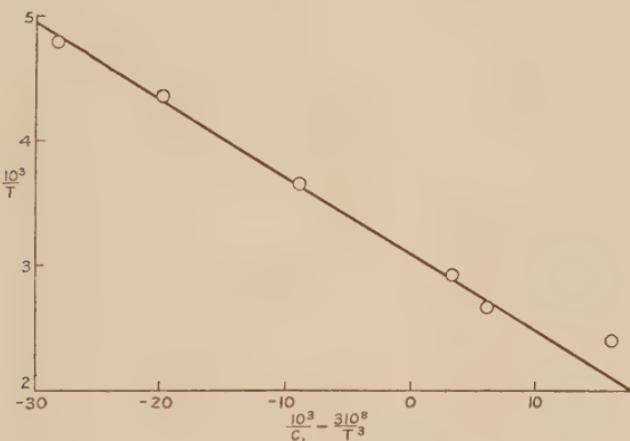
point out, it predicts a negative adsorption at high temperatures.

Great interest attaches to equation (4). Since

$$\frac{d\left(\dfrac{\Delta F_0}{RT}\right)}{dT} = -\frac{\Delta H_0}{RT^2}, \quad \frac{\Delta F_0}{RT} = \frac{\Delta H_0}{RT} + \text{constant}$$

if we take ΔH_0, the change in heat content, as invariant with temperature. Hence we should have

$$\log c_1 c_2 = \frac{\text{constant}}{T} + \text{constant}.$$

When $\log c_1 c_2$ is plotted against $\frac{1}{T}$ we do, in fact, get a straight line, except at low temperatures (fig. 2). In fig. 2

·5 has been added to the ordinates for CO_2, in order to separate the curves.

Thus the experimentally observed variation of c_1 and c_2 with temperature can be given a theoretical basis ; conversely, the use of a virial equation in two dimensions is supported.

Fig. 2.
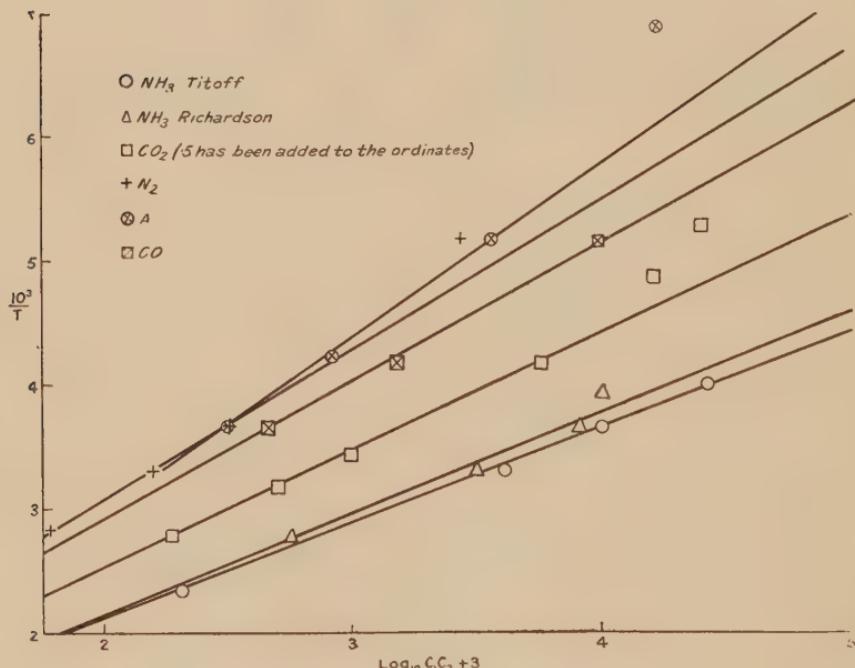
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The University, Leeds.
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LX. *Oscillations in Discharge-Tubes and Allied Phenomena. By* Sir J. J. Thomson, *O.M.*, *F.R.S.* *

Summary.

This paper consists of two parts: the first is a theoretical investigation of the behaviour of an ionized gas under the conditions existing in a discharge-tube. It is shown that the electrons will oscillate with a high frequency, their oscillations producing alternating currents of this frequency. It is also shown that under certain conditions the discharge through the positive column, whether it is striated or continuous, should be intermittent.

The second part contains a description of experiments made to investigate these effects. The method used was to examine the discharge by a rapidly rotating mirror. Intermittence or oscillation shows itself by a series of bright lines separated by intervals depending on the speed of the mirror. I have examined many types of discharge, and found that whether they are produced by a battery of cells or an induction coil they always between certain limits of pressure and current show intermittence. The appearance in the rotating mirror looks very much like a spectrum made up of three types of lines, which I call α, β, γ. The α lines occur when the pressure and current are such that dE/di is negative where E is the E.M.F. and i the current; they represent a series of explosions following each other at regular intervals which increase when a Leyden jar is put in parallel with the discharge-tube.

The β lines I think are due to the intermittence in the positive column already alluded to; they are much nearer together than the α lines, from which they also differ in that they are not affected by the addition of a jar to the discharge-tube.

The γ lines are always close to the α lines; they are very close together, and therefore represent vibrations of far greater frequency than the α or β lines. I think they correspond to vibrations of the ionized gas excited by the disturbance which produces an α line. Like the β they are not affected by connecting a jar up to the tube.

In addition to these effects, there is another, which I have called "throbbing," somewhat similar in character to the α effect though on an entirely different scale. It is got most easily when the distance between the anode and cathode is but a little greater than the length of the Crookes dark space. The discharge passes for a time, then stops, and after an interval begins again, and may go on doing this for half an hour or more. I have known the intervals between the luminous flashes to be as long as a minute, though usually they are much shorter. I attribute "throbbing" to an effect similar to that which produces polarization when a current passes through a liquid electrolyte.

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THE experiments described in this paper were commenced with the object of studying the electrical oscillations in an ionized gas. It can be shown (J. J. Thomson, Phil. Mag. vi. p. 1254, 1928) that when the pressure is so small that the motion of the ions is not affected appreciably by the molecules of the gas through which they are passing the ions vibrate with the frequency $c\{Ne^2/m + N'e^2/M\}^{\frac{1}{2}}\pi^{\frac{1}{2}}$; N and N' are respectively the number of electrons and positive ions per unit volume, m the mass of an electron, M' that of a positive ion, e the electronic charge, and c the velocity of light. As the experiments progressed it was found that, though oscillations could be observed in the electric discharge through gases in almost every case when the pressure was low, these oscillations were of very different types and arose in different ways. Some of these were of the same character as the intermittent discharge through a neon tube; there were others with quite different characteristics, and some of these were, I think, due to the oscillations of the ionized gas in the tube.

Intermittences in the electric discharge under a constant potential difference seem to have been first observed by Gassiot in 1863; they have since been made the subject of many investigations, of which an excellent account is given by Valle (Phys. Lect. xxvii. p. 473, 1926). More recent investigations have been made by Appleton and West (Phil. Mag. xlv. p. 879, 1923), Neumann, *id.* xlvii. p. 939, 1924), R. E. Clay (*id.* l. p. 985, 1925), Whiddington (Proc. of Royal Inst. xxv. p. 67, 1926). Direct

experiments on the oscillations of dense streams of electrons in mercury vapour have been made by Yonks and Langmuir (Phys. Review, xxxii. p. 195, 1929), who estimated the frequency of some of the vibrations they observed to be as high as 10^9.

Properties of an Ionized Gas Exposed to Electric Forces.

When an electric discharge passes through a rarified gas mixtures of electrons and ions are found in various parts of the discharge, *e. g.*, the negative glow and the positive column. As such mixtures can be thrown into vibrations, and as such vibrations are not taken into account in the ordinary theory, it is essential to consider some of their consequences. I will take a case where the mathematical treatment is very simple—that of a slab

Fig. 1.
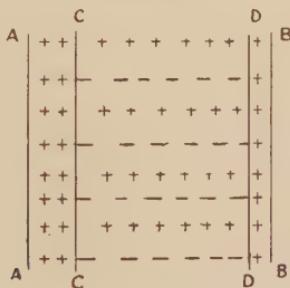
of ionized gas between two large parallel insulated metal plates A and B (fig. 1). Suppose that a uniform electric field is produced suddenly between the plates by giving a charge of electricity of surface density $-\sigma$ to A and one of $+\sigma$ to B. Then at first, before the ions and electrons have had time to adjust themselves, there is a uniform electric force $4\pi\sigma$ between the plates tending to move the electron, in the direction $\Lambda \rightarrow B$. We shall suppose that the negative electricity is carried by electrons and that in comparison the positive ions move so slowly that their motion may be neglected to a first approximation.

Let X be the electric force in the direction $\overline{AB}$ at a point P distant x from A ; then if u is the velocity of the electrons at P, and N their number per unit volume, $Neu\,\delta t$ units of negative electricity pass in the time δt through

unit area of a plane through P at right angles to x. This will produce a change δX in X, where

$$\delta X = -4\pi N eu \,.\, \delta t.$$

Thus

$$\frac{dX}{dt} = -4\pi N eu. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If ξ be the coordinate fixing the position of an electron, $u = d\xi/dt$. If the pressure of the gas is so low that the motion of the electrons may be regarded as free $m\,du/dt = Xe$. Substituting this value of X in (1) we have

$$\frac{d^2u}{dt^2} = -(4\pi N e^2/m)u,$$

and if N does not vary with the time,

$$\frac{d^2X}{dt^2} + (4\pi N e^2/m)X = 0.$$

Thus

$$X = X_0 \cos pt, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $p^2 = (4\pi N e^2/m)$; X_0 is the initial value of X. equation (1) shows that dx/dt vanishes when $t = 0$.

If ξ_0 is the value of ξ when $t = 0$, and $d = X_0/2\pi N e$,

$$\xi = \xi_0 + \frac{d}{2}(1 - \cos pt); \quad . \quad . \quad . \quad (3)$$

d is the amplitude of vibration of the electron. Under the action of the electric force the electrons will begin by moving away from the cathode A, and there will be a space next A devoid of electrons which requires special treatment. Its boundary is the plane reached by the electrons which started from A, and is given by

$$\xi = \frac{d}{2}(1 - \cos pt).$$

When $x \ngtr \xi$ the force at x is given by

$$X = X_0 - 4\pi N e\,x,$$

and does not vary with the time. The electrons move through the distance d; all within this distance of the plate B will be driven against it. If B is insulated and there is no reflexion of electrons, it will receive a negative charge equal to dNe, i. e., $X_0/2\pi$. The original positive

charge on B was $X_0/4\pi$, so that at the end of the first movement of electrons towards B the charge on it has been reversed and $-\sigma$ is now the charge on both electrodes. In the gas between the plates there is a positive charge equal to 2σ. The charges on the plates will remain constant, as no electron (if its motion is entirely controlled by the electric forces) will reach the plates with finite velocity.

Representation of Motion of Electrons.

The state of things can be represented by supposing that all the electrons are in a slab CD (fig. 1) whose faces are parallel to A and B and whose thickness is $(l-d)$, and that this oscillates backwards and forwards between the plates with the frequency p; the amplitude of excursion of the slab is $d = X_0/2\pi Ne$. The force inside this slab is uniform and equal to $X_0 \cos pt$.

Distribution of Force between the Plates.

If X is the force at a point distant x from A, when ξ is the distance of the boundary C of the slab from A, then, if $AB = l$,

$X = X_0 - 4\pi Nex$; from $x = 0$ to $x = \xi$,

$X = X_0 \cos pt$; from $x = \xi$ to $x = \xi + (l-d)$,

$X = X_0 \cos pt - 4\pi Ne(x - (\xi + l - d))$; from $x = \xi + l - d$ to l.

From these values we can show that the potential difference between A and a point at a distance x from it is, if $x < \xi + l - d$,

$$\tfrac{1}{4}X_0 d \sin^2 pt + X_0 \cos pt . (x - \xi).$$

The potential difference between A and C (fig. 1) is $(X_0/4) d \sin^2 pt$, that between C and D, $(l-d)X_0 \cos pt$, that between D and B is $-(X_0/4)d \sin^2 pt$, that between A and B is $(l-d)X_0 \cos pt$. The mean value of the potential difference between A and a point at a distance x from it is $X_0 d/8$, while the maximum value is $X_0 x$, which, when x is large compared with d, will be large compared with the average value.

Analogy of this Distribution with that in a Discharge-Tube.

The regions between A and C and between D and B have properties analogous to those of the Crookes dark space;

the electrification in these is always positive, the force in them is a linear function of the distance from the electrode, and the potential differences between A and C and B and D never change size; all these are properties of the dark space. The properties of the space between C and D resemble those in the negative glow, since there is no excess of one kind of electricity over the other, while the time average of the electric force is zero.

Lower Limit to the Frequency of the Vibrations.

If l is less than d there can be no vibrations, as all the electrons are driven out of the gas before their motion is reversed.

Since $p^2 = 4\pi N e^2/m = 2Xe/md$, it must be greater than $2Xe/ml$, or if V is the initial potential between the plates than $2Ve/ml^2$. If v is the velocity acquired by an electron in falling through this potential $2Ve = mv^2$, so that $p > v/l$. Thus the time of vibration must be less than the time taken by an electron to travel over the distance $2\pi l$.

Energy acquired by the Electron.

The kinetic energy of an electron in the region CD is $mu^2/2$, where u is the velocity of the electron.

Since

$$m\frac{du}{dt} = X_0 e \cos pt \; ; \; u = X_0 e \sin pt \,. \,/pm,$$

and the kinetic energy of one of the electrons is

$$\frac{e^2}{2}\frac{X_0^2 \sin^2 pt}{mp^2} = \frac{X_0^2}{8\pi N}\sin^2 pt = e,$$

half the potential difference between A & C.

The maximum value of this is $X_0^2/8\pi N$, which is equal to the maximum value of the electrostatic energy per unit volume divided by N. If this maximum value exceeds $V_0 e$, where V_0 is the ionizing potential of the gas, the electrons will ionize by collision and N will increase. The smaller the value of N the greater is the energy of an individual electron, and hence the greater the chance of ionization by collision and an increase in N. This effect will prevent the energy of the electrons from differing

much from $V_0 e$ and will make N approximate to the
value given by the equation

$$X_0^2/8\pi N \approx V_0 e.$$

The left-hand side is, as we have seen (p. 701), the mean
value of the potential fall at the electrode; thus this fall
would approximate to V_0 and would depend only on the
ionizing potential of the gas and not upon the intensity of
the electric field or upon the pressure of the gas. We see
too that when things are in a steady state the average
kinetic energy of the electrons is equal to the average
electrostatic energy, each being reckoned per unit volume.

Plates not Insulated.

We have supposed that the plates A and B are insulated,
so that the electrons driven against B remain there. If,
however, B is not insulated the negative electricity which
goes up to it will escape by the leads and will not exert
any repulsive force on the electrons between A and B.
In this case it is easy to see that the first effect is to drive
a charge of negative electricity equal to $X_0/2\pi$ through
the lead from B. The electrons left behind will oscillate
to and fro with the amplitude $X_0/2\pi Ne$, but B will be the
end of the excursions of the electrons, and no electron
will strike against B and flow away through its lead.
The current through the lead will stop. If, however,
there is, as there is in the case of the positive column of
the electric discharge, a flow of slow electrons from the
negative glow or Faraday dark space through A into AB,
these will neutralize the positive charge left in AB and
restore to AB as many electrons as had escaped through
the lead at B. These will restore AB to its initial state,
and the stages which were gone through on the first
application of the force will now be gone through again.
A negative charge equal to $X_0/2\pi$ will pass again through
the lead from B, and again there will be no further current
through it until the loss of electrons has been replaced
as before by electrons coming from the negative glow.
Thus in this case, as in the former, a periodic current whose
period is $2\pi/p$ goes through the gas, but now there is what
there was not before, an intermittent current passing
through the leads, the interval between consecutive pulses
being the time taken to restore to the positive column the
electrons taken out of it by the first pulse.

Case of Localized Ionization.

Hitherto we have supposed that the ionized gas filled the whole of the space between the electrodes. We shall now consider the case when the ionization is originally confined to a limited part of the field.

Let the initial ionization be localized in the region between the planes LL and MM, and suppose that the field of force is the same as before. As soon as the field is applied the electrodes will begin to move across MM out of the slab.

The force on the electrons left behind will diminish, and when the electrons originally in a thickness $d/2$ of the slab have been driven across MM the repulsion they exert on those behind them will drive these back into the slab, where they will oscillate with the frequency p and with the amplitude d, where d as before equals

Fig. 2.
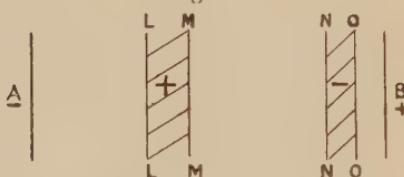
$X_0/2\pi Ne$. The slab LM will be left with a charge of positive electricity equal to $X_0/4\pi$.

Consider now the electrons which have been drawn out of the slab; they will leave it with a small velocity, since they have only moved through a short distance. After leaving the slab they will be accelerated by the electric force, and their velocity will increase until they have moved through a distance s such that

$$X_0 es = V_0 e - (\text{energy of electrons when they left the slab}),$$

where V_0 is the ionizing potential of the gas. They will then begin to ionize by collision, losing their energy as they do so, and in this way another slab NO of ionized gas will be formed; this will have an excess of negative electricity equal to the charge taken from LM. In NO a process similar to that which occured in LM will go on; the same number of electrons that left LM will leave NO, the electric force in NO and the electrons left in it will oscillate, and the electrons ejected from it will form another ionized slab PQ, and so on.

Thus the original slab LM will give rise to a series of other ionized slabs NO. PQ at about equal intervals apart : in fact. the state of affairs will resemble that in the striations of the positive column of a discharge-tube. The negative charge passes from one of these slabs to another. as if going over stepping-stones. Inside these slabs of ionized gas the electric force will oscillate: to the left of L it will remain constant. while between two of these striations, *e. g.*, between M and N. it will vanish. Throughout this investigation we have supposed that the motion of the positive ions is so small compared with that of the electrons that its effect may be neglected.

The interval between two of the striations of ionized gas is V_0/X_0. The distance through which the ionized slab in one of the striations moves during a vibration is $X_0/2\pi Ne$; thus, unless $X_0/2\pi Ne$ is less than V_0/X_0, the striations will overlap and there will be no definite intervals between them. In the case we are considering a negative charge $X_0/4\pi$ jumps from one patch of ionization to another. and finally escapes through the anode ; while this process is going on there will be a current of electricity passing through the striated part of the discharge. After the escape of the negative electricity by way of the anode the system of striations will. if we neglect recombination and the movement of positive ions in comparison with that of electrons be in a steady state. There will be no further emission of electrons from the striations and there will be no current through the gas. In the striations there will be local currents oscillating with the frequency p. The electric force vanishes between the striations.

This state of things cannot, however, continue, since in a discharge-tube there is a stream of electrons coming from the negative glow and the Faraday dark space towards the first striation: those coming up to LM will neutralize its positive charge and restore it to the condition it was in before it had emitted any electrons. The process we have just described will recommence, charges of negative electricity equal to $X_0/4\pi$ will spring from one striation to another, and there will be a fresh discharge of electricity through the gas; this, as before, will be followed by a period when there is no discharge, and this again by another when there is a discharge: thus the discharge along the positive column will be intermittent. The *minimum* interval between two discharges will be of the order of

the time taken to give to LM a negative charge equal to $X/4\pi$. If ι_0 is the average current through the negative glow this time will be of the order $X/4\pi\iota_0$. If s is the distance between two striations X will be of the order V_0/s, where V_0 is the ionizing potential of the gas. Thus the minimum time interval between two discharges will be of the order

$$\frac{V_0}{4\pi s\iota_0}.$$

For hydrogen $V_0 = 12$ volts $= \cdot 04$ in electrostatic measure. When the discharge is '' normal '' ι_0 (see p. 710) at the pressure of 1 mm. is 9×10^{-5} amps. $= 27 \times 10^4$ electrostatic units, and s is about 1 cm.; the minimum time is thus

$$\frac{1}{\pi \times 27 \times 10^6}.$$

At a pressure of $\cdot 01$ mm., when $\iota_0 = 27$ and $s = 10$ cm., this interval would be $1/\pi \times 27 \times 10^3$, which is of the same order as that indicated for some of the vibrations in my experiments.

The values given for ι_0 refer to the region in the cathode dark space; they are not true in other parts of the discharge unless the geometrical conditions are such that the current density is constant between the anode and the cathode. When the area of the cross-section of the tube is greater than that of the cathode the density may be less than the normal value and the intervals longer than the values given above.

The time $X/4\pi\iota_0$ is that required to neutralize the positive charge on the first striation; it would not represent the interval between two discharges if in addition to neutralizing the positive charge the ionization in the first layer had to be renewed owing to recombination between the electrons and positive ions.

The preceding refers to intermittence and not to electronic oscillation. We can form an estimate of the frequency of the oscillations in the normal glow discharge when the electrodes are two large parallel plates in the following way. When the discharge is '' normal '' the current passing through unit area in the gas is a definite quantity which is proportional to the square of the pressure of the gas and depends upon the nature of the electrodes and the kind of gas in the tube. The value of this

current, ι, for aluminium electrodes and nitrogen at a pressure of 1 mm. of mercury was found by Günther-Schulze (*Zeit. für Physik*, xx. p. 1, 1923) to be $38\cdot4 \times 10^{-5}$ (amp./cm.^{2}), or in electrostatic measure $\iota = 115\cdot2 \times 10^4$. In the negative glow, where there are as many electrons as positive ions, the current will be carried practically entirely by electrons, so that

$$\iota = \mathrm{N}ev,$$

where v is the average velocity of the electrons. As the average electric force is exceedingly small in the glow, v can hardly be much greater than 10^8; taking v as 10^8 and $\iota = 115\cdot2 \times 10^4$, $\mathrm{N}e = 115\cdot2 \times 10^{-4}$, and $4\pi\mathrm{N}e^2/m = 8 \times 10^{16}$, and the frequency about $4\cdot5 \times 10^7$. Since the current i is proportional to the square of the pressure, the frequency will be proportional to the pressure, and thus at the pressure of $\cdot1$ mm. would be $4\cdot5 \times 10^6$. The frequencies I observed at these pressures were much smaller than this, being more nearly of the order 10^5 at a pressure of about $\cdot2$ mm.

The following is another method of estimating the frequency of the electronic vibrations in the positive column.

We have seen (p. 703) that owing to ionization by collisions the number of electrons per unit volume may be expected to approach the value N, given by the equation

$$8\pi\mathrm{N} = \frac{\mathrm{X}_0{}^2}{\mathrm{V}_0 e}.$$

Since

$$p^2 = 4\pi\mathrm{N}e^2/m,$$

we have

$$p^2 = \tfrac{1}{2}\frac{\mathrm{X}_0{}^2 e}{m\mathrm{V}_0}.$$

In the positive column X_0 is proportional to the pressure; thus the frequency of the vibrations will be proportional to the pressure. This equation leads to values of p of the same order as those just given.

Oscillations in the Crookes Dark Space.

When there are N′ positive ions and N electrons per unit volume the frequency of their oscillations is

$$(\mathrm{N}e^2/m + \mathrm{N}'e^2/\mathrm{M})^{\frac{1}{2}}/\pi^{\frac{1}{2}},$$

where M is the mass of the positive ion, m that of the electron. Since M is so much greater than m the positive ions have not much influence on the frequency of the oscillations unless there is a great preponderance of positive ions over electrons, and hence a large positive charge. The Crookes dark space is one where there is such a preponderance. The period of the oscillations in this space may be determined as follows:—Let C (fig. 3) be the cathode, NN the boundary of the dark space, the electric force is a minimum in the neighbourhood of NN, between C and NN there are very few electrons and a nearly uniform distribution of positive electricity. To the right of NN the density of the electrons increases rapidly, and ultimately becomes nearly equal to that of the positive ions. There is a flow of positive ions from right to left across NN; let u_0 be the velocity of the

Fig. 3.
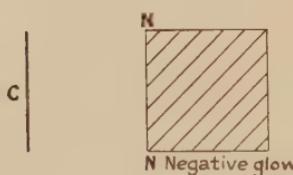
positive ions just on the right of NN in the steady state. Suppose that owing to some disturbance u_0 is changed to u, then in the time δt there is an increase in the positive charge between C and NN equal to $\rho(u-u_0)\delta t$, where ρ is the density of the positive ions at NN. This will produce a change δX in the electric force at N, δX being given by the equation

$$\delta X = -4\pi\rho(u-u_0)\delta t\ ;$$

thus

$$\frac{dX}{dt} = -4\pi\rho(u-u_0),$$

but

$$M\frac{du}{dt} = Xe,$$

where M is the mass of the positive ion. Hence

$$M\frac{d^2u}{dt^2} + 4\pi\rho e(u-u_0) = 0,$$

or, since

$$\frac{du_0}{dt} = 0,$$

$$M \frac{d^2(u-u_0)}{dt^2} + 4\pi\rho e(u-u_0) = 0 ;$$

there will thus be oscillations having the frequency

$$\frac{1}{2\pi}\left(\frac{4\pi\rho e}{M}\right)^{\frac{1}{2}} = \frac{1}{2\pi}\left(\frac{4\pi N e^2}{M}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (4)$$

if N is the number of positive ions per unit volume. If V is the cathode-fall of potential, l the thickness of the dark space, we have, assuming Aston's law that the density of the positive electrification in the dark space is constant,

$$V = 2\pi \cdot \rho l^2.$$

Substituting this value for ρ, we see that the frequency is equal to

$$\frac{1}{2\pi} \cdot \left(\frac{2V \cdot e}{l^2 M}\right)^{\frac{1}{2}}.$$

If $\frac{1}{2}MU^2$ is the energy acquired by the positive ion in falling through the dark space, $2Ve = MU^2$; hence the frequency is equal to $U/2\pi l$. The dark space is thus a stable system and when disturbed vibrates with a frequency directly proportional to the pressure. The density of the positive ions in the dark space is much greater than that of the electrons in the positive column, and this to some extent balances as far as the frequencies of the oscillations are concerned the effect of their much greater mass.

The frequencies of the oscillations of systems of electrons and ions depend only upon the number of these per unit volume and the masses of the ions, they do not depend upon circumstances external to the discharge-tubes, such as the capacities of condensers attached to its electrodes. This distinguishes them from some of the many forms of oscillation which are revealed when the discharge-tube is observed on a rotating mirror. We have from Günther-Schulze's experiments the material for calculating the frequencies of the vibrations of the dark space.

Günther-Schulze (*Zeit. für Physik*, xx. p. 1, 1923) gives the following values for V in volts and l the thickness

in cm. of the dark space at the pressure of 1 mm. of
mercury, where the cathode is made of aluminium :

	V.	L.	$(e/M)^{\frac{1}{2}}$.	$\iota \times 10^5$.	Frequency.
He	153	1·32	$6·52 \times 10^6$	1·072	$1·03 \times 10^6$
Ne	145	·637	$3·78 \times 10^6$	1·81	$·95 \times 10^6$
Arg	150	·285	$2·70 \times 10^6$	14·07	$1·5 \ \times 10^6$
N_2	215	·305	$4·55 \times 10^6$	38·4	$2·8 \ \times 10^6$
H_2	192	·724	17×10^6	9·00	$4·4 \ \times 10^6$
O_2	250	·237	$4·25 \times 10^6$	54·7	$3·7 \ \times 10^6$

The frequencies calculated by equation (4) are given in
the fifth column.   The frequency is directly proportional
to the pressure.   Observations with a revolving mirror
(described later on) showed this effect very distinctly,
and though it was not found possible to determine
accurately by this method the frequency of the oscillations,
it was at pressures about ·1 mm. between 10^5 and 10^6 in
hydrogen and carbonic acid.   The oscillations in the dark
space involve oscillations in the number of positive
particles striking against the cathode per unit time.   There
are good reasons for thinking that the impact of these
particles is largely responsible for maintaining the dis-
charge, so that oscillations in the number of impacts
would produce fluctuations in the rest of the discharge,
and thus the effect of the oscillations will not be confined
to the immediate neighbourhood of the cathode.

Another cause which may produce intermittence is
that under certain conditions $d\mathrm{E}/di$ may be negative,
where E is the potential difference between the terminals
of the discharge-tube and i the current through the tube.
This is the same cause as that which produces the inter-
mittence of neon tubes and the singing arc.

Consider the case when the terminals of a discharge-
tube T (fig. 4) are connected with those of a battery B
of storage cells and also by short leads with the plates of
a condenser C.   When, as in the experiments described
in this paper, the battery circuit has great self induction
and resistance oscillating currents will only flow through
it with great difficulty.   Such currents flowing through
the discharge-tube will complete their circuit by flowing
into the condenser instead of round the battery circuit.
If the self inductance and the resistance of the leads to

the condenser are negligible, E, the potential difference between the terminals of the tube will also be that between the plates of the condenser. If i is the alternating part of the current through the tube, and x the charge on one of the plates of the condenser,

$$i + \frac{dx}{dt} = 0 ;$$

but

$$E = \frac{x}{C},$$

or

$$\frac{d\,E}{dt} = -\frac{i}{C}.$$

Fig. 4.
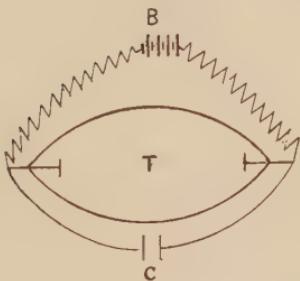
But

$$\frac{d\,E}{dt} = \frac{d\,E}{di}\frac{di}{dt} ;$$

hence

$$\frac{di}{dt} = -\frac{1}{C \cdot d\,E/di} \cdot i,$$

or

$$\iota = (\text{constant})\epsilon^{-\int \frac{dt}{C \cdot d\,E/di}}.$$

If $d\mathrm{E}/di$ is negative then any disturbance produced in the tube will increase, and after a time measured by $C \cdot d\mathrm{E}/di$ the disturbance will reach an intensity sufficient to produce an explosive discharge in the tube; this may sweep away the ionized gas from between the electrodes, and the discharge will be interrupted. The original distribution of electric charges in the tube will be built up again by the battery, a new disturbance will form, this

will increase as before and produce a fresh explosive discharge, and so on. There will thus be a succession of these discharges following each other at intervals measured by $C . \frac{dE}{di} + T$, where T is the time taken to build up the field, T will be proportional to C, and so will therefore be the interval between two successive discharges. If the discharges were viewed after reflexion from a rotating mirror the increase in the interval would show itself as an increase in the distance between the images representing these discharges. Thus the distance between the lines representing discharges of this type would be increased by connecting capacity to the discharge-tube, while this would not affect the distance between the lines representing discharges of the types considered previously. This theory is confirmed by the following experiment :—the relation between the

Fig. 5.

α (pressure 3·6mm) β. (pressure 1·1mm.) γ (pressure ·5mm)
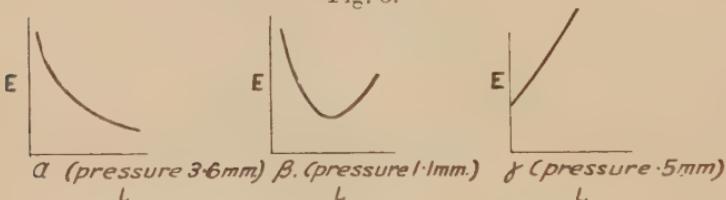
potential difference between the electrodes and the current through a discharge-tube was plotted for the discharge through hydrogen at a considerable number of pressures. The graphs for pressure 3·6, 1·1, and (·5) mm. of Hg are represented in fig. 5, α, β. γ respectively ; the ordinates represented potential differences, the abscissæ current.

In α, dE/di is negative for all values of the current, and at this pressure the discharge always showed lines which were affected by the addition of capacity to the tube. In β dE/di is negative only when the current is small, and for this pressure the discharge only showed lines sensitive to the addition of capacity when the current was small ; for larger currents the oscillations were not affected by capacity, had a much greater frequency, and were of a different type. In γ, dE/di is always positive, and the oscillations were not affected by adding capacity whether the current through the tube was small or large.

The distance between the lines representing the oscillations increased as the current diminished ; this is what

might be expected. as T, the time of restoration, will be greater for weak currents than for strong.

The preceding consideration of the properties of ionized gas has led us to recognize the possibility of several types of vibrations in a discharge-tube. These may be classified as follows :—

(1) The vibrations of the electrons themselves depending only upon the number of electrons per unit volume. In the normal discharge the frequency is proportional to the pressure of the gas ; the frequency is high. exceeding 10^6. unless the pressure of the gas is less than that due to 1 mm. of Hg. These vibrations depend only upon the conditions inside the tube. and are not affected when a condenser is connected up with the tube.

(2) The vibrations of positive ions. These are similar in character to (1). though, owing to the much greater mass of the ions. the frequency *ceteris paribus* is not so great. They will only occur when the number of ions is greatly in excess of that of electrons. as it is in the Crookes dark space at the cathode.

(3) This is the type last considered. of which the intermittent neon lamp is an example. This is not a harmonic vibration like (1) and (2). but rather a series of explosions following one another at regular intervals. This type is affected to a very great extent by connecting a condenser up with the tube.

(4) We have seen that under certain conditions the discharge along the positive column, whether continuous or striated. might be expected to become discontinuous. the interval between successive discharges depending on the rate at which electrons diffuse from the negative glow into the positive column. These vibrations resemble (3) in being a succession of pulses rather than a harmonic vibration. They differ, however, from (3) in not being affected when a condenser is connected up with the discharge-tube. It is only in discharges of types (1) and (2) that the current changes its direction. In types (3) and (4) it is intermittent, but always in one direction.

Experiments on the Oscillations.

The first method I used to study the oscillations in the discharge was one in which the intermittence of type

(3) plays a very important part. It is an experience familiar to all who have worked on discharge through gases that at certain pressures, when the discharge-tube is directly connected with the pump, the luminosity is not confined to the tube itself, but spreads through the whole system of tubes connecting it with the pump and the McLeod gauge. A short discharge-tube may thus produce luminosity several metres away from the tube itself. This supplies a useful method of getting a column of ionized gas in a position which may be specially convenient for observation.

The reason for the spread of luminosity I take to be somewhat as follows :—The conditions in the discharge-tube are such that $d\mathrm{E}/di$ is negative, so that the discharge consists of a series of explosions. An explosion raises the pressure of the gas in the discharge-tube, and the ionized gas rushes out through all the exits from the tube. The tubes leading from the discharge-tube are thus filled with ionized gas through which a discharge can pass easily. The mechanical effects of these pulses can easily be observed by inserting in one of the tubes connected with the discharge-tube a light vane mounted like the vane of a radiometer ; this, when the pressure is not too low, is set in rotation when the discharge passes between the electrodes in the discharge-tube.

The pulses which accompany intermittent sparks have been photographed by Töpler * and Mach †. Foley ‡ measured the velocity of propagation, and found that near the spark it was much greater than the velocity of sound, but soon became normal ; when the pulse is constrained to pass through tubes the velocity is greater than in the open. Hertz § observed under certain conditions something shaped like a vortex ring travelling comparatively slowly from the positive electrode.

I used the following method to study the luminosity spreading out from the discharge-tube:—

The discharge passed between two electrodes about 2 cm. apart in a discharge-tube AB (fig. 5) ; long lengths of quill tubing were fixed on to this tube ; part of this went to the pump ; there were in addition lateral branches

* Töpler, Pogg. *Ann.* cxxxi. pp. 33, 80 (1867) ; cxxxiv. p. 194 (1868).
† Mach, *Wien. Ber.* lxxvii. (2) p. 819 (1878).
‡ Foley, Phys. Review, xvi. p. 449 (1920).
§ Hertz, Wied. *Ann.* xix. p. 87 (1893).

which provided a system of blind alleys. The length of tubing connected with the discharge-tube was in some of my experiments as much as 10 metres. The discharge was produced by a large induction coil whose secondary was connected with the electrodes A, B ; a rectifier was inserted in series with the discharge-tube. The coil and the rectifier were placed in a large metal box, and all the leads from the coil to the discharge - tube passed through earthed metal tubing. When the pressure is high the discharge is confined to the tube AB, but when it falls below a certain value a luminous discharge passes through the tubing connected with AB ; this discharge may under favourable circumstances fill several metres of carefully insulated tubing. A much-branched system

Fig. 6.
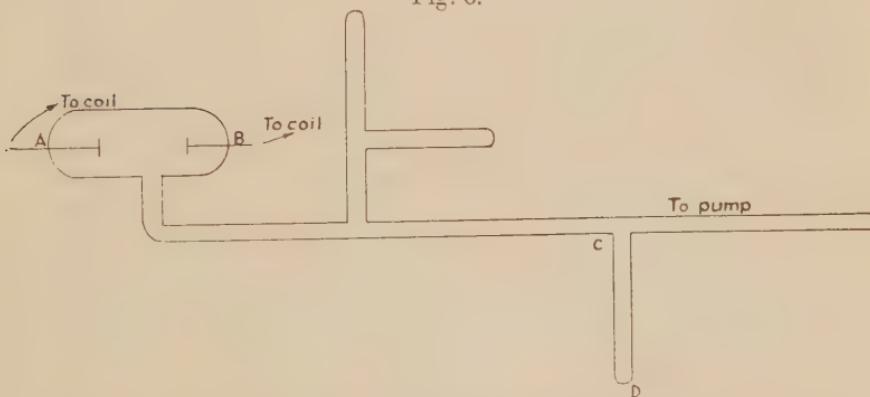
of tubes such as that connected with AB will have all the lateral shoots as well as the leaders full of luminosity. If some of these laterals are provided with taps which can cut off their connexion with AB, turning the tap not only stops the luminosity in its lateral but also produces a marked increase in that of the rest of the system. This suggests that the discharge between A and B produces a disturbance which rushes through all the available channels, and if some of them are closed the disturbance which went previously through them is diverted to the others.

The luminosity can also be stopped by applying a strong transverse magnetic force to the tube ; this produces the same effect as turning a tap. The magnetic force must be strong enough to drive positive ions as well as

electrons against the walls of the tube. This requires a tube of small bore, so as to reduce the air gap in the magnetic field. The luminosity may pass freely down the tube when there is no magnetic force but be stopped when a strong magnetic force is excited. These observations show that the luminosity requires a free passage for gas and ions between the discharge-tube and the place where it occurs.

If a wire is fused into the system of tubes connected with the discharge-tube the luminosity on the side of it remote from this tube is very much enfeebled when the wire is connected with earth or with a condenser of considerable capacity.

The Luminosity is traversed by Alternating Currents.

The luminous discharge through this system of tubes is of an exceedingly interesting character. Take, for example, a side tube like CD (fig. 6), carefully insulated and treated so as to prevent any creeping of electricity over its surface. The discharge in it is often not merely a uniformly luminous column, but one showing all the characteristics of an ordinary discharge between electrodes, such as striations and a dark space at the end of the tube. Careful observation shows that there are two sets of striations with their concavities pointing in opposite directions, and that the end of the tube shows not only a dark space characteristic of the cathode but also traces of the anode glow ; this suggests that the discharge through these blind alleys is an exceedingly rapidly alternating current, showing the characteristics of normal currents through gases.

That this is so is shown quite unmistakably by the following experiments :—The side tube CD (fig. 7) is exposed at EF to a strong magnetic field produced by placing the poles of an electromagnet on either side of the tube, so that the magnetic force is at right angles to the plane of the paper. Then when the electromagnet is not excited the discharge has the appearance shown in fig. 7, while when the magnet is on the discharge near the magnet is concentrated into two bright lines, one pressing against the top of the tube, the other against the bottom, as in fig. 8 ; these lines are traversed by a large number of striations very closely packed together. These sharp lines are streams of electrons ; this can be proved by observing their deflexion

when the magnetic field is altered by moving a permanent
magnet near them: the direction of motion of the electrons
in one stream is opposite to that in the other.   In the
parts of the field not quite close to the magnet the discharge
is not so concentrated as it is between the poles, and in
these regions for a certain range of pressures the discharge
is striated, showing the appearance represented in fig. 8.

Thus there are two discharges, each showing the charac-
teristics of the normal discharge between two electrodes.

Fig. 7.
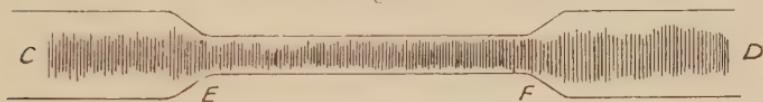
The resemblance is made even more striking if a flat disk,
connected to earth or to a condenser, is fused into the
end of the tube: then at certain pressures when the mag-
netic field is on, one half of this disk will show all the
characteristics of a cathode, *i. e.*, dark space, negative glow
and so on, while the other half looks like an anode showing
the positive glow.   Thus the disk acts like a cathode at
one time and an anode at another.   The distance between
the striations observed in the side tube and the thickness
of the dark space at the disk are the same, or very nearly
the same, as the distance between the striations and the
thickness of the dark space in the normal discharge

Fig. 8.
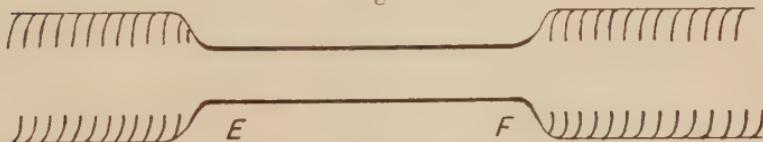
between electrodes in a gas at the same pressure and in a
tube of the same diameter.

The oscillatory character of the discharge may also be
shown by wrapping round the tube a piece of tinfoil
and connecting this with one of the terminals of another
discharge-tube containing gas at a low pressure, the other
terminal being put to earth.   This second tube is not
sealed on to the main tube, and the gas in it is at a constant
pressure.   When the main tube gets filled with luminosity
the auxiliary one is traversed by a discharge, but the
effects are the same at each of its terminals: for example,

each exhibits the Crookes dark space and the negative glow, showing that the discharge is oscillatory.

A closer study of the division of the glow discharge by magnetic force into two currents flowing in opposite directions reveals some interesting features. The current flowing in one direction is much brighter and less deflected by the magnet than the one in the opposite direction. The striations are more conspicuous in the more easily deflected one than in the other. In helium the two portions are of different colours, the more easily deflected one being tawny and the other greenish blue. The direction of the magnetic deflexion as well as the curvature of the striations shows that the direction of motion of the electrons in the more easily deflected current is towards the spark-gap AB, which is connected with the induction coil and is the origin of the discharge. Its direction does not depend upon the direction of the main current between A and B, thus it is not affected by reversing the coil, though this produces minor changes in the appearance of the discharge.

The following experiment gives, I think, a clue to the explanation. The experiment was tried with helium, and the part of the tube where the magnet force was applied was wide enough to permit of the two portions being so widely separated that by screens one could be cut off and the other observed by itself. The tube was arranged so that these two portions were vertical, and they were observed in a mirror rotating about a vertical axis. When the blue portion was cut off the appearance in the mirror was that of a number of equally spaced yellow lines. When, however, the yellow part of the discharge was cut off and the blue portion observed there was a blue line to be seen, but this was followed by a number of yellow lines at equal intervals, similar to those seen when the yellow portion of the discharge was observed in the rotating mirror. I think this indicates that the brighter and less deflected portion of the discharge contains the first portion of the discharge, due to the spread of an explosion through the tube from the spark-gap, and that this excites vibrations in the ionized gas in the tube, and that these are indicated by the series of yellow lines which are observed whichever part of the deflected current is covered up. Without the aid of the mirror these yellow lines in the less deflected portion are masked by the greater

brilliancy of the pioneering discharge through the gas. I was once, when conditions were favourable, able to get indications of this without the use of the mirror. In fig. 9 the two yellow portions, A, B are seen, as well as the less deflected central portion C.

Experiments on Electrical Oscillations.

The method I have used in by far the greater number of the experiments is to observe the discharge after reflexion from a rotating mirror whose axis is parallel to the discharge. If the discharge is continuous the appearance in the mirror is a band of continuous luminosity ; if, however, it is intermittent or oscillatory, the mirror will show a series of lines separated by intervals proportional to the time of oscillation or the interval between two discharges. These electrical oscillations are influenced

Fig. 9.
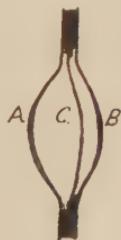
by so many conditions, such as the intensity of the current, the nature and pressure of the gas in the tube, the presence of impurities, the shape of the electrodes and the material of which they are made, the state of their surface, the effects of hysteresis, etc., that the subject is an extremely complicated one. It is difficult to make sure that in two different experiments all these conditions are the same. The effects observed vary so much and so rapidly that when one first approaches the subject it is desirable to use a method which will show at a glance what is happening, even though it is not so well adapted for making exact measurements as others which take much longer to apply and to interpret.

I have used two mirrors in these experiments, a small one very carefully made and which can run up to about 200 revolutions per second ; the upper limit of frequencies

of lines which can be separated by this is about 5×10^5 under good conditions.

The dispersion obtained with this mirror is so great that the time interval between two lines which can be observed simultaneously in the mirror cannot be greater than 10^{-4} sec. Thus a series of lines separated by intervals greater than this would appear as detached lines when observed in the mirror, and there would be nothing to indicate that they were members of a series. The high-speed mirror is useful for working out the details, but not for making a general survey. For this purpose I used a very much larger mirror, which could run up to about 10 revolutions per sec., and gave very much brighter images than the small mirror run at the same speed.

Care is necessary in interpreting the origin of lines seen in rotating mirrors, as sometimes owing to imperfections in the surface of the mirror the image of a continuous source of light will appear to be traversed by dark spaces, as if it were discontinuous. These spurious lines can easily be differentiated from those due to intermittence in the discharge, as the latter are affected when a magnet is brought near the discharge-tube, while the former are not.

In all the experiments I have made on the discharge of electricity through gases I have always, when the pressure of the gas and the current passing through it were within certain limits (the limit for the current depending on the pressure), found that the discharge was oscillatory or intermittent. This is so whether the discharge is pro-duced by a battery of storage cells, by an induction coil, by a constant voltage dynamo, or by the discharge of a hot tungsten filament connected with a battery of cells. In these the oscillations, though they may differ in detail, show the same characteristics. A very convenient method of studying them is to use a tube where the cathode is a tungsten filament heated by a small insulated battery and the anode and cathode of the tube are connected with the terminals of a battery of storage cells or a constant voltage dynamo. There is a constriction in the middle of the tube to concentrate the light of the discharge. The tube was viewed in the larger mirror rotating about 10 times per second.

If hydrogen in the tube is at the pressure of a millimetre or so of mercury, and the voltage applied to the tube is gradually increased until a discharge begins to pass, the

appearance of the tube as seen in the revolving mirror is
that of a series of fine lines (fig. 10), equally spaced and
exceedingly close together, stretching right across the field
of view, indicating oscillations with frequencies of tens of
thousands of vibrations per second; at this stage no change
is produced by connecting the electrodes of the discharge-
tube with a large Leyden jar. When the potential diffe-
rence is gradually increased, and with it the current, a
stage is reached when the appearance of the discharge

Fig. 10.

changes with dramatic suddenness. The image in the
mirror (fig. 11) is now crossed by a series of very bright and
sharp lines (α lines), and between these α lines the lines
seen in the previous stage (β lines) were visible, though
faint. The frequency of the oscillations corresponding
to the α lines is at most but a few per cent. of that corre-
sponding to the β lines. The insertion of a Leyden jar
in parallel with the discharge-tube, which produces no
effect on the β lines, produces a great increase in the

Fig. 11.

distance between the α lines, and this increase seems to be
a linear function of the capacity of the jar.

On still further increasing the voltage the brightness
of the α lines increases for a time, but the lines disappear
suddenly when the voltage reaches a certain value. With
voltages above this value the appearance is like that of the
first stage—nothing except β lines can be seen in the field
of view. In this stage, as in the first, the addition of the
Leyden jar produces no effect.

There is generally a patch of luminosity alongside each
α line, on that side of the line which shows that it occurs

later than the line itself. Examination by the rapidly
rotating mirror shows that this luminosity consists of a
number of fine lines very close together, the distances
between them corresponding to frequencies from 10^5 to
10^6. We shall call them γ lines ; they are represented in
fig. 12. When the capacity of the discharge-tube is small
enough to let the α lines come fairly close together, the
intervals between them may be quite filled by the γ lines,
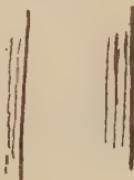
Fig. 12.

and the discharge has the appearance represented in fig. 13,
while when there is greater capacity it looks like fig. 12.

The distances between consecutive α, β, or γ lines
increase as the pressure diminishes. In helium the α
lines are bluish and the β and γ tawny ; the γ lines corre-
spond to the easily deflected parts of the discharge
in long tubes described on p. 718, the α lines to those
which are not so easily deflected. This is shown by the

Fig. 13.

fact that when the image of the discharge in the con-
stricted part of the tube looks like fig. 13 the application
of the transverse magnetic force drives off all the γ lines
and leaves only the α lines, as shown in fig. 14. If in the
preceding experiments we were to keep the E.M.F. on
the tube constant, and increase the current by increasing
the temperature of the filament, the same changes are gone
through as the temperature rises as those produced when
the E.M.F. is increased and the temperature kept constant,
i. e., at first there are only β lines, then when a certain

temperature is reached the α and γ lines appear, at a still higher temperature there are again nothing but β lines. Or, again, if we keep both the E.M.F. and the temperature constant, but gradually reduce the pressure, we find that at the pressure when the discharge begins to appear the β lines are the only ones to be seen; as we go on reducing the pressure a stage is reached when the α and γ lines suddenly appear : these persist through a considerable range of pressure and then die out, and only β lines are to

Fig. 14.

be seen. These are often done up into groups separated by dark spaces as is indicated in fig. 15.

These results are in accordance with the view that the α lines represent an intermittent discharge of type 3 (p. 713); they are not harmonic oscillations, but a series of consecutive explosions. The γ lines are of type 1, and are the vibrations of ionized gas excited by these explosions, while the β lines are of type 4.

An interesting effect often observed in these discharges is that, when the discharge has the appearance of fig. 13,

Fig. 15.

if a specially bright discharge flashes through the tube the image of the discharge is followed by a large black patch devoid of all luminosity, instead of as in fig. 13 by the γ lines. This, I think, is due to the explosion being so violent that all the ionized gas is driven out of the path of the discharge, carrying away with it the material which produced the luminous lines. This effect bears a striking resemblance to the " black " flashes which are sometimes seen in photographs of thunderstorms.

Additional evidence as to the origin of the α lines is afforded by observations in the rapidly rotating mirror

when the discharge is in such a state that, though the great majority of the lines are β and γ lines, some α lines do come in, though at long intervals. The appearance of an α line is accompanied by a disturbance of the β and γ lines which immediately follow it ; before the α line came into sight these were straight lines, after its appearance they are turned into intricate curves. The effect is especially marked if a jar be connected with the discharge-tube. It is often quite an appreciable time after the appearance of the α line before the other lines recover their original appearance ; this is what we should expect if the α line corresponds to an explosive discharge.

With a very strong discharge the α line is no longer straight, but is followed by streamers like those shown in fig. 16.

The disturbance produced by an α line on the γ lines near it varies within very wide limits. In some cases,

Fig. 16.

as we have seen, it destroys all luminosity in its neighbour-hood, in others it bends the adjoining γ lines into all sorts of kinks and curves. Sometimes, however, the effect is much less violent, and the γ lines are still straight but on the slant instead of vertical.

Motions of Striations down the Tube.

The rapid motion of striations from anode to cathode under certain conditions, which was originally discovered by Spottiswoode, and investigated more recently by Aston and Kikuchi, seems to me to be an effect of the same kind. When observing the appearance of a vertical striated column in a mirror rotating about a vertical axis I found that up to a certain pressure the image in the mirror showed a series of horizontal lines, as it would if the striations were steady, as the pressure was lowered these got tilted, the direction of the tilt depending on that

of the current through the tube ; this is the Spottiswoode effect. As the pressure was reduced still further a stage was reached when the lines became vertical, and were the lines due to the intermittence of the discharge. The pressure at which the tilt began was about the pressure when the α lines just began to appear in the tube, suggesting that the motion of the striations was due to the puffs produced by the explosive discharge which caused the α lines.

In addition to the large black patch following a very strong α line, there may be observed at certain pressures a series of well-defined more or less regularly spaced dark lines at the end of the luminous patch which correspond to a single α line. This effect is represented in fig. 17. This suggests that the discharge represented by the

Fig. 17.

S. Black Spaces. *d* line.

patch of luminosity becomes itself intermittent as it is dying away. When the whole of the discharge from cathode to anode is in the field of view, it is found that some of these black bands do not stretch from cathode to anode but are only to be found in one part of the tube, generally the constricted part, and that the regions near the cathode or the anode or both of these are still luminous, indicating a certain independence of the various parts of the discharge. This is shown more clearly by observing the luminous parts of the discharge by the aid of the rapidly revolving small mirror. In many cases the intervals between the lines in one part of the discharge-tube are not the same as between those in another part. They may not be the same close to the cathode as they are in the middle of the discharge-tube or close to the anode. There are thus several frequencies in the tube. The relative magnitudes of these frequencies may vary with the shape

of the electrodes, the pressure of the gas, and the intensity of the current. In some cases the lines are closer together at the cathode than at the anode, in others they are more widely separated. Some of the lines seem only to exist close to either the cathode or the anode, while a large number seem to stretch right across the tube. Thus the conclusions to which we are led by the study of the bright lines agree with those suggested by the behaviour of the dark one.

The existence of vibrations of different periods in different parts of the discharge is also shown by the following experiment. A discharge-tube (fig. 18) with C A as electrodes is connected with the pump by a long length of quill tubing which is bent back so that a portion

Fig. 18.
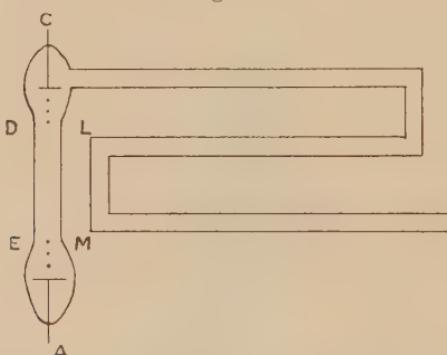
LM is parallel and side by side with the positive column DE in the discharge. The images of LM and DE can be seen simultaneously in the revolving mirror. When the tube was filled with hydrogen at the pressure of ·017 mm. and a discharge from an induction coil sent between A and C the β and γ lines were well developed in both DE and LM, but the intervals between them were greater in LM than in DE, *i. e.*, the frequencies of the vibrations were greater in DE than in LM. This is what we might expect, as the density of the ionization is greater in ED than in LM and the frequency increases with the density.

Electrodeless Discharge.

The bright ring discharge which occurs when a bulb filled with gas at a low pressure is surrounded by a coil of wire traversed by the very rapidly alternating currents

produced by the discharge of a Leyden jar is of considerable interest in connexion with the oscillations. The discharge forms an endless ring, so that there are no electrodes, no dark spaces, and as the electrons travel round closed paths they are not removed from the ring, and thus have not to be replaced. Thus of the types of intermittence given on p. 718 the only one for which the conditions exist in the electrodeless discharge is the vibrations of a mixture of ions and electrons. I examined by the rotating mirror the ring discharge in mercury vapour and in CO_2 at various pressures. A vertical slit was placed in front of the bright ring and the light coming through it examined by the mirror. The appearance was quite different from that of the other types of discharge. In the great majority of cases all that was to be seen was a single bright and quite sharp line accompanied by a luminous band in which I was never able to be sure that I could see any separation even when the mirror was run at the highest speed it would stand, though once or twice I suspected them. If the band is made up of γ lines they are much closer together and therefore correspond to higher frequencies than the other types of discharge. This is not to be wondered at, as we know that the momentary currents in the ring discharge rise to very high values; thus the maximum density of the ions in the path of the discharge would be very high and their frequency very great. On a few occasions a few feeble lines were seen as well as the bright ones. I attribute these to oscillations in the circuit producing the oscillating currents in the coil round the bulb.

Throbs in the Electric Discharge.

I shall now describe some phenomena which are met with in the electric discharge which in some respects resemble those associated with the α lines, though the period of intermittence is on quite a different scale. When an electric current from a battery of storage cells is sent through a tube where the electrodes are two equal parallel disks and the upper one connected with a winch, so that the distance between the electrodes can be altered without altering the gas, the following effects are observed.

Let us suppose that at first the distance between the electrodes is much greater than the thickness of the dark

space. If we lower by the winch the upper electrode the diminution in the distance between the electrodes at first produces little diminution in the deflexion of a galvanometer placed in series with the battery and dischargetube. When, however, the upper electrode gets so close to the lower that only a small thickness of the negative glow is left between the cathode and the anode the current diminishes very rapidly as the distance between the electrodes diminishes, and it only requires a very small further diminution in the distance to stop the discharge altogether. In the short interval between the beginning of the rapid diminution in the current and its extinction as the cathode is very slowly lowered the current becomes intermittent. It stops for a time and begins again, and may go on doing this for hours if the circumstances are favourable. The tube behaves very much like an intermittent neon tube ; the gas, however, need not be neon. I have obtained the effect with all the gases I have tried—hydrogen, helium, nitrogen, oxygen, argon, and CO_2; it is obtained especially easily in helium and CO_2. We shall call this visible intermittence of the discharge '' throbbing.'' When the distance between the electrodes first reaches the value at which the throbs begin these follow one another very rapidly ; when the electrodes are brought a little nearer together the current through the tube diminishes and there are fewer throbs in the same time. The throbs get slower and slower as the distance diminishes, the current gets less and less, and finally stops. This sometimes occurs without altering the distance between the electrodes. This is an example of a very important effect which occurs under certain conditions, viz., the gradual diminution of the current with the time when the potential difference is kept constant. We shall return to this subject later on. A large number of factors influence the throbbing ; one of these is the electrification of the walls of the dischargetube. When a tube is throbbing touching it with a finger will alter the rate and may even stop it altogether. The effect depends upon how long the finger is held against the tube ; thus, for example, if the tube is throbbing once a second and the finger held against the tube for one second the throbbing may recommence almost as soon as the finger is removed, if it is held for five seconds throbs may begin again after ten seconds, and if it is held for ten seconds the throbbing may not begin again at all. If a ring of

tinfoil is pasted round the outside of the tube the rate of throbbing will change according as the ring is insulated, earthed, or connected to the anode or to the cathode.

The discharge when the distance between the electrodes approximates to the length of the dark space is extraordinarily sensitive to external influences, and might possibly be of use as a detector. For example, a very small diminution in the pressure of the gas produces a great diminution in the current, and may even extinguish it : this is readily explained by the increase of the dark space due to the fall of pressure bringing the electrode into this space. This also explains why warming the tube with a small gas jet diminishes and may even stop the current. If a pad of cotton wool dipped in liquid air is placed against the tube in the neighbourhood of the electrodes, so as to cool the gas in the tube, the first effect is to increase the current ; this is due to the increase in density. This, however, is soon followed by a diminution in the current, and often by its extinction. This is due to the freezing out of some constituent of the gas, generally a trace of water vapour, which, though present only in small quantities, has an enormous effect on the current through the gas under these conditions. We shall return to this point later.

Again, when the electrodes are as close together as they are in these experiments, the current depends to a very large extent on the condition of the electrodes A and B. Even when these are made of the same metal and treated in the same way the current for the same E.M.F. is different when A is cathode and B anode from what it is when A is anode and B cathode. It is generally possible to adjust the distance between the electrodes so that the current will pass in one direction but not in the opposite.

Differences such as these are naturally increased greatly when the electrodes are made of different metals. It very often happens that the tube can easily be got to throb when the current is in one direction, while it is almost impossible to get it to do so when the current is reversed. A tube with one electrode made of nickel and the other of aluminium may throb when the latter is cathode, but not when it is anode. Anything which affects the magnitude of the current also affects the throbbing ; thus, for example, when the tube is filled with helium and connected with the pump it will often throb when there is a liquid

air-trap to prevent the mercury vapour from the pump getting into the tube, but will not do so when this is absent.

The interval between the throbs may be more than a minute, and is thus of quite a different order from that between the discharges which give rise to the α lines.

Polarization at the Electrodes.

A characteristic feature of the discharge between two electrodes separated by a distance but little greater than the thickness of the dark space is the diminution in the current which occurs after the E.M.F. is first applied.   The current does not remain constant but diminishes rapidly at first and then more slowly.   Sometimes it diminishes to zero, at others it reaches a certain value and then remains steady.   In the early stages the current may have been too large for throbbing, but as it diminishes it reaches a stage

Fig. 19.
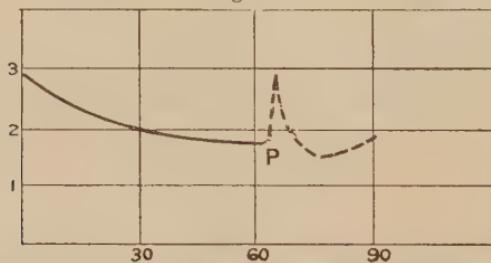
Hydrogen pressure ·2 mm.; ordinates current in milliamp.; abscissae time in minutes; current reversed at P; ordinates in dotted curve represent magnitude of reversed current.

when the throbs appear; as the current still further diminishes the intervals between the throbs become longer and longer, and either reach a finite value or the discharge goes out.   The time taken by the discharge to reach a steady state is very considerable, often more than an hour. The effect was observed with H_2, O_2, N_2, CO_2, and helium. It is of the same character as that which occurs in liquid electrolytes owing to the polarization of the electrodes. The analogy is increased by the behaviour of the current through the gas when the E.M.F. is reversed.   The reverse current starts with a high value, then diminishes very rapidly, the diminution reaches a maximum, and then the current begins to increase.   The graph (fig. 19) represents the relation between the current and the time for a discharge through hydrogen at a pressure of ·2 mm.

The current after it is reversed often shows periodical fluctuations before settling down into a steady state. An example of this is shown in the graph (fig. 20), which represents the relation between the current and the time after reversal of a discharge through hydrogen at a pressure of ·32 mm. of Hg ; the potential difference applied was 1000 volts and the electrodes were aluminium disks 1 cm. apart.

Observations with the revolving mirror also indicate polarization, for after the reversal of the current the distribution and intensity of the lines is for a few moments one that is not seen under steady conditions whichever way the current is passing.

I think the polarization manifested by the effects observed after the reversal of the current suggests an explanation of the throbbing. Near the electrodes there

Fig. 20.
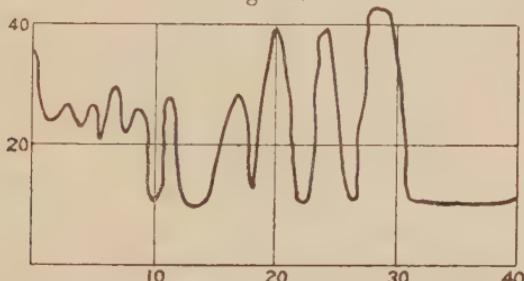
Hydrogen pressure ·27 mm. ; ordinates in milliamp. ;
abscissæ in minutes ; 1000 volts between terminals.

will be a distribution of electricity both in the gas and also on the walls of the tube which will, like the polarization in a liquid electrolyte, produce a counter electromotive force and diminish the current. The polarization may increase so much that the current falls below that required to maintain the discharge, and the discharge stops. The distribution of charged ions which produced the polarization will tend to disappear unless continually removed by fresh ions and electrons produced by the electric discharge; so that, if the discharge stops, the polarization will begin to diminish and with it the counter electromotive force. It requires, however, a considerably greater E.M.F. to start the discharge after it has been extinguished than to maintain it after it has once been started, so that the counter E.M.F. will have to diminish by a considerable

amount before the discharge starts again. As this diminution is caused by the dispersion of charged particles near the electrodes this will take an appreciable time, and during this time there will be no luminosity in the tube ; this will correspond to the dark part of the throb. When the counter E.M.F. has diminished so much that the discharge can start again the luminosity will reappear. The current will, as before, run down owing to the increase of the polarization until it again vanishes, and the process will be repeated.

The polarization at the cathode will depend upon the ease with which the positive ions give up their charges to the cathode. The more easily this occurs the more difficult it will be to build up the polarization and, *ceteris paribus*, the greater the duration of the luminous part of the discharge.

The transfer of the charge on an ion to the metal of the cathode is greatly influenced by gas films on the metal, by the kind of metal used for the cathode. and upon the kind of gas in the tube ; all these things as we have seen influence the throbbing.

Part of the counter electromotive force is due to the electrification upon the walls of the tube near the electrode. and the amount of this will depend upon the shape and size of the discharge-tube and the distance of the electrodes from its walls. The appearance of luminosity in the tube when touched by the finger several seconds after the discharge has stopped, shows that this electrification disappears very slowly. The slowness of this is shown also by the experiment described on p. 728, which shows that the large effects produced when the tube is touched by the finger require the contact to be maintained for several seconds.

Again, the rate at which the polarization is produced might be expected to depend upon the size of the electrode. I have found it very much easier to get the tube to throb when one of the electrodes is a small aluminium sphere and the other a disk than when both are disks.

The throbbing depends on so many variables that it is not surprising that its character changes apparently capriciously and that the alterations observed when the pressure is diminished from a high to a low value are often not repeated in the reverse order when the pressure is increased to its original value. This capriciousness is very apparent

in the effect produced by adding the capacity of a Leyden jar to the discharge-tube. In many cases the addition of the jar produces no appreciable effect on the interval between the throbs; the appearance of the throbs sometimes changes suddenly and the interval between successive ones becomes much shorter, and now may be greatly increased by the addition of the jar. This, I think, is in accordance with the view we have taken of the origin of the throbs. The formation of the double layer which produces the polarization will cause the tube itself to have increased capacity. If the two sides of the double layer are very near together the tube will have a large capacity which may be much greater than that of the jar: in this case the jar will not affect the intervals. If, however, the two sides of the double layer are much further apart the intrinsic capacity of the tube may be comparable with that of the jar, and now the interval between the throbs will be increased by the jar. In a few cases the addition of the jar increased the rate of throbbing, but was accompanied by a change in the character of the discharge and was not permanent.

The Effect of Cooling the Gas in the Discharge-Tube by Liquid Air.

A discharge-tube, when the distance between the electrodes is just a little greater than the thickness of the cathode dark space, is in such a sensitive state that it furnishes a very convenient means of studying the effects of small changes in the conditions of discharge. One of the changes I have studied in this way is that of cooling the discharge-tube by applying to its surface a pad of cotton wool dipped into liquid air. If the discharge produced, say, by a battery of small storage cells had got into a steady state, the application of the pad produced a large diminution in the current passing through the discharge-tube, reducing it sometimes to a small fraction of its original value. When the pad, after having been for some time in contact with the tube, was removed the current began to increase, slowly at first, but afterwards with great rapidity, the current rising far beyond its value before the pad was applied. It then began to decline, and sank to its initial value.

I next tried whether a pad applied near the electrodes would produce any effect if the tube had already been

cooled by liquid air. To try this a tube which could be dipped into liquid air was fused on to the discharge-tube at some distance from the electrodes. The tube was filled with helium at the pressure of ·79 mm. ; before dipping the side tube into liquid air the deflexion of a galvanometer in series with the discharge-tube was 400, when the side tube was dipped into liquid air the current dropped suddenly to 53, and after three-quarters of an hour became steady at 42, the pressure now being ·78. When a liquid air pad was put against the tube close to the electrodes, the side tube being all the time in liquid air, the current dropped to 31, on taking off the pad it rose to 78, and finally became steady again at 41.

I next tried dipping one end of the discharge-tube into liquid air, so that the liquid air was close to the electrodes. The current was not affected now by putting a liquid air pad against the tube, but when the liquid air was removed from the tube there was such a great increase in the current that the spot of light from the galvanometer went right off the scale and the discharge blazed out for a time with great luminosity. It is evident that something which greatly facilitates the discharge is condensed by the liquid air against the walls of the discharge-tube. The large current following the removal of the liquid air rapidly dies away, which suggests that the gas which is condensed readily goes to the electrodes and forms polarized layers which give rise to a counter E.M.F. I tried to get some information about the nature of this gas by sealing on to the discharge-tube three spectroscopic tubes (1), (2), (3), and sealing (1) off before the liquid air was put on, (2) while the liquid air was on, and (3) after the liquid air had been taken off and while the large current was going through the tube. I took photographs of the spectra in these tubes, which Mr. Newall was kind enough to measure up. The chief difference between them was the much greater brilliance of the hydrogen lines in (3) than in either of the others. The simplest explanation of this seems to be that the gas is mainly water vapour. A very small quantity of this must produce a great effect, for, as we have seen, when a side tube was kept in liquid air a pad dipped in liquid air and pressed against the tube produced a further diminution in the current.

I measured the current through the tube at intervals of five seconds after taking off the liquid air ; the result is represented in the graph (fig. 21) where the abscissæ

represent the time after the removal of the liquid air and the ordinates the current.

No effect seems to have been produced until after 90 seconds, when the glass has become sufficiently warm for the most volatile of the deposits to distil off ; after this has gone there is a lull in the rise of current until the temperature rises to that at which the most important impurity begins to distil over. The graph indicates that there are two volatile constituents condensed by the liquid air, CO_2 ? and H_2O ?, of which the least volatile is the more important. For other experiments on the substances

Fig. 21.
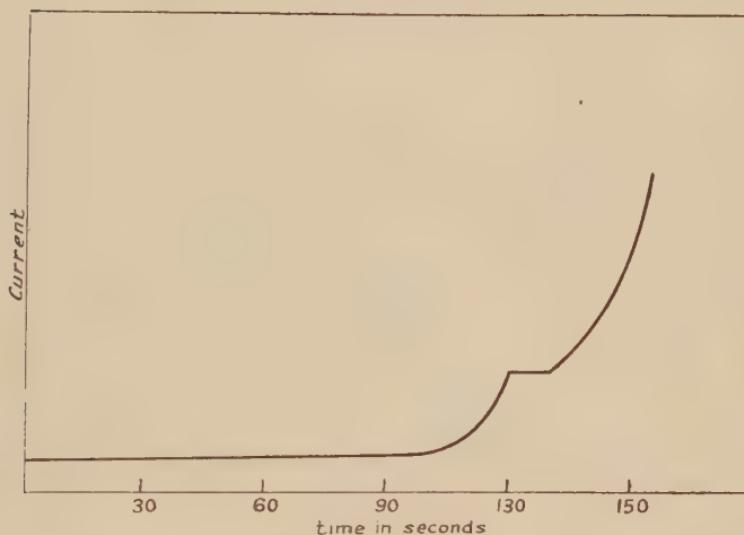
condensed by liquid air from discharge-tubes reference may be made to a paper by the author published by the Société Française des Electriciens, Paris, 1927.

The substances which produce this effect are present in the gas when the discharge is not passing through it, and are not manufactured by the current. This is shown by the fact that if the pad is put against the tube before the discharge begins and taken off just before it starts the current rises to as great a value as it would do if the current had been passing all the time the pad was pressed against the tube.

I have much pleasure in thanking Mr. Everett and Mr. Morley for the assistance they have given me in making these experiments.

LXI. *Application of the Wynn-Williams Bridge Valve Amplifier to Microphotometry and Absorption Problems. By* H. G. HEIL, *Department of Physics, Ohio State University, Columbus, Ohio* *.

A VERY sensitive valve amplifier for detection of minute currents has been described by C. E. Wynn-Williams [1] [2]. An excellent description of the bridge arrangement used and a discussion of the best working conditions are to be found in these two articles.

Fig. 1.
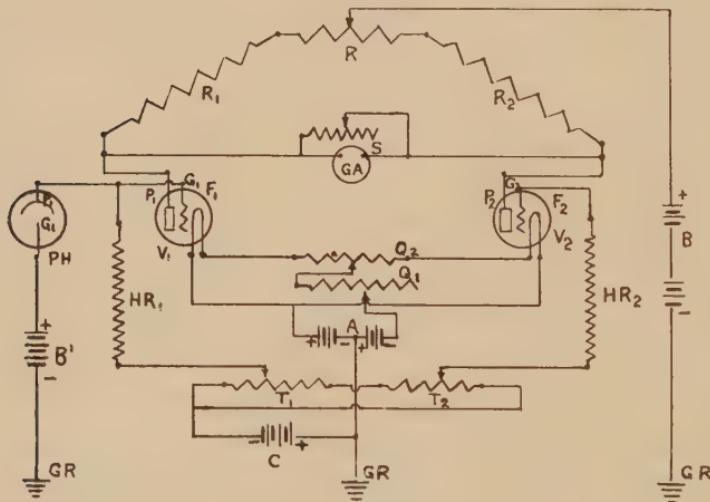
The possibility of using the amplifier as a detector of photo-electric currents is suggested by Wynn-Williams. This suggestion has also been made and applied by Razek and Mulder [3] [4]. These investigators have studied very carefully the best working conditions of the bridge, and have been able to secure very high amplification [5].

Recently in this laboratory the bridge amplifier has been used as a high sensitivity microphotometer, and a direct comparison of the results thus obtained was made with the results found by using a Moll recording microphotometer.

The simplified electrical diagram of the arrangement used is given in fig. 1, and is for the most part like that

explained in detail by Razek and Mulder and by Wynn-Williams. No detailed explanation therefore is necessary. HR_1 and HR_2 are xylol or xylol-alcohol resistances. The order of magnitude seems not to make very much difference in the adjustment and final sensitivity attainable, except that they should be approximately equal in order to secure steadiness of the zero reading. In use all parts of the arrangement must be very well screened from external disturbances. In fact, the best arrangement is one in which all adjustments can be made from a position remote from the metallic shield. Failure to observe these precautions results in false estimates of currents.

The results herewith presented were obtained by Mr. O. C. Woodyard and Mr. F. W. Pote. An emission spectrum plate of magnesium, which was prepared by Mr. S. F. Essig in this laboratory, was mounted on a pair of fairly accurate ways. It could be moved laterally across the active plate P^1 of the photo-electric cell Ph in steps of ·025 mm. In front of this plate was a very narrow slit, and about 20 cm. in front of the slit and plate a single filament tungsten lamp was placed.

The results obtained from two widely separated portions of this plate are shown in figs. 2 and 3. The results found with the Moll recording microphotometer on the same portions of the plate are also shown as insets on the same figures. Some parts of the curves found with the Moll instrument have been retouched in order to make them a little more easily seen. This does not apply, however, to any of the peaks. It will be seen from an inspection of these curves that the Wynn-Williams bridge amplifier when carefully used gives results which are not at all inferior to those of the Moll microphotometer. It is to be noted that, with the exception of a single point in the regions of the plate which were studied, the deflexions of the galvanometer were many times the least one which could be read with accuracy. In this connexion it may be said that the limit of sensitivity was by no means reached, since the Leeds and Northrup type P galvanometer which was used was shunted throughout with a 10 ohm coil. Also the amount of light actually entering the photo-electric cell could have been increased several fold. It has been estimated that all galvanometer readings are accurate to less than 1 mm., and that the steady drift of the zero or dark reading

Fig. 2.

Motion of Plate 1 unit = ·025 mm.

Fig. 3.

Motion of Plate 1 unit = 025 mm.
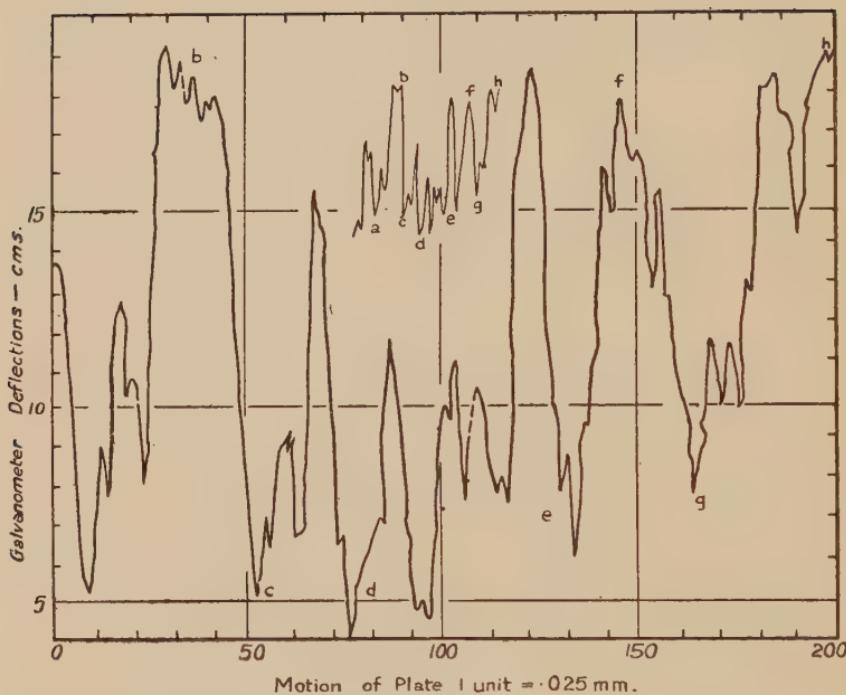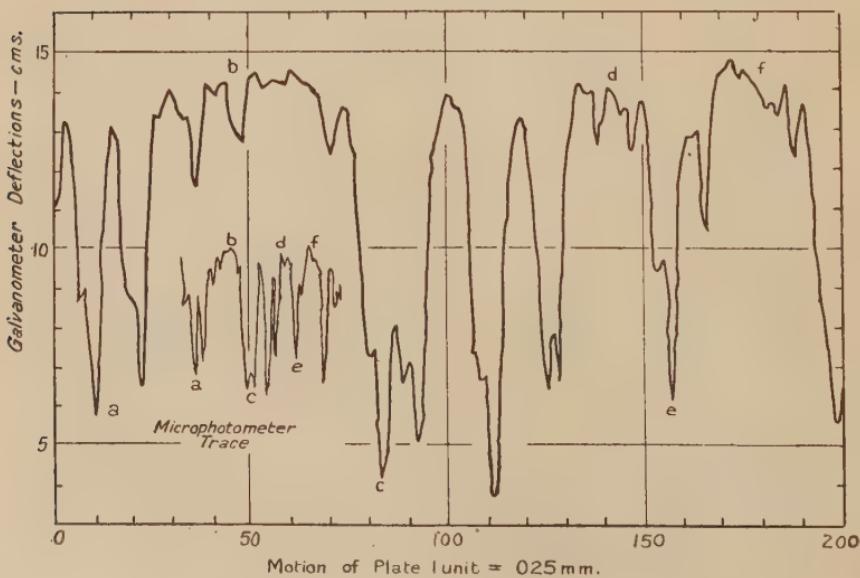
occurring during a time of about one hour while the observations in fig. 2 were recorded, was not in excess of 1 mm.

For convenience in comparing the records the letters *a, b, c,* etc. have been printed on corresponding parts of the curves. It will be seen that the present arrangement shows all of the structure given by the Moll record, and in some cases seems to indicate a structure which is difficult to see in detail on the latter. Indeed, on two portions of a very poor photographic spectrum plate it was possible to obtain an excellent record with the

Fig. 4.
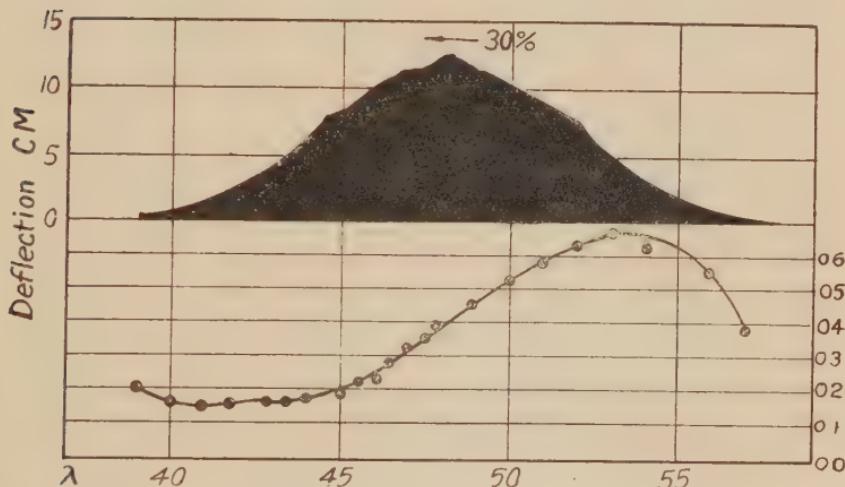
valve amplifier bridge, whereas no records whatever were obtained when the same portions of the plate were run through the Moll microphotometer in the usual way.

By mounting an absorption chamber and Hilger direct reading monochromator in front of the photo-electric cell it is possible to obtain absorption curves of non-fluorescent solutions. When rather large steps on the wave-length scale of the monochromator are used it is not possible to show any structure of an absorption line, but the general character of the absorption curve may be obtained with considerable accuracy. The results obtained on one such solution by Mr. Pote are shown in fig. 4. The upper curve shows the absorption of fuchsin as a function of wave-length, while the lower curve gives the relative

absorption coefficients as calculated by the usual relation

$$\mu d = \log_\epsilon \frac{I_0.}{I}.$$

I_0 = intensity of light before absorption,

I = intensity of light after absorption by the filter, corrected for absorption of the glass cell,

μd = mass absorption coefficient.

Throughout the work described here and other work which will be reported shortly the grid G_2 of the second or inactive valve has been earthed through the high resistance HR_2. In some previous work G_2 was left " floating." This latter method is the arrangement used by Wynn-Williams. It has been the experience of the writer that a high resistance leak to ground from the grid of the inactive valve makes the entire arrangement somewhat less subject to external disturbances, and also renders the zero reading somewhat more steady. It seemed doubtful at the time these experiments were made whether any scheme of compensation could make the steady drift much smaller than that found on account of inevitable alterations in the valve characteristics with time. However, while these experiments were in progress, Razek and Mulder [5], by very careful study of all factors contributing to unsteadiness of the zero, have succeeded in making the zero drift independent of all changes. As a matter of fact, a steady drift quite in excess of that recorded above can occur, and corrections can be made so as to render the error on account of it quite inappreciable.

The minimum current actually recorded on a type P Leeds and Northrup galvanometer of normal sensitivity about 10^{-8} ampere per scale-division was approximately 10^{-13} ampere. It is to be recalled, however, that this sensitivity was secured with a shunted galvanometer. The limit of sensitivity is even less than this figure.

References.

(1) Wynn-Williams, Proc. Camb. Phil. Soc. iii. (1927).
(2) Wynn-Williams, Phil. Mag. (7) vi. (1928).
(3) Razek and Mulder, Phys. Rev. xxxiii. (1929).
(4) Mulder and Razek, Phys. Rev. xxxiii. (1929).
(5) Razek and Mulder, Journ. Opt. Soc. Amer. (December 1929).

LXII. *Studies in Coordination.*—Part III. *The Energy of Coordination. By* F. J. Garrick, *B.A.*[*]

1. *Introductory.*

IN the preceding papers[†] of this series an attempt was made to explain the formation of ion hydrates and ammino compounds on an electrostatic basis. From the known electrical properties of the water or ammonia molecule, and with the aid of certain assumptions as to their repulsive force constants, the (negative) potential energy of various hydrates or ammines was calculated. This was denoted by ϕ, and with the assumption that minimum ϕ (maximum energy evolved) corresponds to the stablest complex ion, the coordination numbers were deduced. In future the energy evolved $(-\phi)$ will be called the Energy of Coordination.

It would be desirable to show how far the values so obtained for the energy of coordination can be justified by comparison with other better established energy quantities, and this is the object of the present paper. We will first consider some of the factors which influence the result of the comparison. Three cases may be distinguished : (i.) The general physical picture of the complex ion may be wrong. This would be so if some electron-sharing linkage (*e.g.*, Sidgwick's Coordinate Link) were involved. In this case agreement, even to order of magnitude, could hardly be expected. (ii.) The general physical picture being correct, the numerical values of the (calculated) energy of coordination might be inaccurate, due to errors in the data employed (such as dipole moments) or in the deduction of the force constants, or involved in simplifying assumptions. The inaccuracy arising from these sources might amount to something like 10 per cent. (The force constants are very uncertain, but a variation of 10 per cent. in these only affects the final result by about 1 per cent.) (iii.) The quantities used in the comparison may be incorrect. This case is of importance, since a direct comparison with experimental quantities is impossible : there must be some admixture of

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theory, and the most we can do is to investigate how far the results of the electrostatic theory of coordination are consistent with those of more general and more firmly established theories. A discussion of the errors involved here is best postponed until the methods of comparison have been explained.

2. *The Lattice Energies of some Ammines.*

The term "lattice energy of an ammine" is here used as meaning the energy difference between one mol of the crystalline ammine and its free gaseous anions and complex ammino-cations *. The term can only be used in this sense when the crystal structure of the salt is known to be such that all the ammonia is present in complex cations of the general form $[M(NH_3)_n]^{Z+}$. For salts fulfilling this condition it is clear that, given the lattice energy and heat of formation of the complex salt and the lattice energy of the simple salt, we can obtain the energy of coordination by means of a cycle. The heat of formation is of course an experimental quantity, and the lattice energy of the simple salt can be obtained thermochemically, but the lattice energy of the ammine can only be obtained theoretically, that is, by calculation according to the Born theory. This requires a knowledge of the crystal structure and molecular volume of the ammine, and then two assumptions are necessary. First, a value must be assumed for the repulsion index operating between the complex cation and the anion. Second, it must be assumed that the configuration of the complex cation is unchanged on passing from vacuo into the lattice. The latter assumption is presumably incorrect, but the energy term corresponding can reasonably be assumed small. The assumption of a value for the repulsion index is very hazardous, but the value must be a large one (greater than 5), and therefore the repulsion term in the lattice energy is small. The value chosen is 9, the number which holds for most simple salts, and the use of this number cannot introduce an error greater than 10 per cent. of the lattice energy. As the lattice energy of the ammine is about half that of the simple salt, the error from this source is probably not greater than the uncertainty of the latter quantity. It thus appears that, granting the correctness of the general physical picture, the energy of coordination may be obtained by the cycle indicated above with an uncertainty which can very roughly be estimated as

* This term has been used in a different sense by other workers (see Biltz and Grimm, *Z. Anorg. Chem.* cxlv. p. 63 (1925)).

about 10 per cent.—of the same order, that is, as the uncertainty of the theoretical value.

The group of hexammine-chlorides isomorphous with $[Ni(NH_3)_6]Cl_2$ is known * to have a crystal structure which is that of a CaF_2 lattice in which each Ca^{2+} ion is replaced by a $[Ni(NH_3)_6]^{2+}$ ion. The molecular volumes of some of the members of this group have been measured by Biltz †, and the force-constants of some of the central cations (necessary for the theoretical energy of coordination) have been given by Lennard-Jones ‡. In the three cases for which all these data are available the cycle can be performed, and the numbers are given in the following table. Here the first column gives the central cation and the second gives U_{MCl_2} the lattice energy of its chloride. This is taken from Grimm and Herzfeld § for $ZnCl_2$ and obtained by the Born cycle ‖ in the other two cases. The third column gives the molecular volume of the ammine, according to Biltz (*loc. cit.*),

1.	2.	3.	4.	5.	6.	7.
Ion.	U_{MCl_2}.	$V_{MCl_2 6NH_3}$.	$U_{MCl_2 6NH_3}$.	$Q_{MCl_2 6NH_3}$.	$-\phi_{obs}$.	$-\phi_{calc}$.
Zn^{2+}	676	159·9	327	89	438	439
Fe^{2+}	634	160·3	327	88	395	423
Mn^{2+}	615	166·2	323	82	374	391

(All energy quantities are in k cal. per mol).

and the fourth column its lattice energy calculated from this by Born's expression for the CaF_2 lattice ($1770 \sqrt[3]{1/V}$, using $n = 9$). The fifth column gives the heat of formation of the ammine from simple salt and gaseous ammonia (Biltz, *loc. cit.*). Then, performing the cycle we obtain the energy of coordination as : $-\phi_{obs} = U_{MCl_2} + Q_{MCl_2 6NH_3} - U_{MCl_2 6NH_3}$. The values so obtained are shown in column 6, and in column 7 are given the theoretical values. These are calculated precisely as described in II., and the details need not be given ;

* Wyckoff, J. Amer. Chem. Soc. xliv. p. 1239 (1922).

† Biltz, *Z. Anorg. Chem.* cxxx. p. 93 (1923) ; Biltz and Birk, *ibid.* cxxxiv. p. 125 (1294).

‡ Lennard-Jones and Dent, Proc. Roy. Soc. A, cxiii. p. 690 (1927).

§ Grimm and Herzfeld, *Z. Physik*, xix. p. 141 (1923).

‖ $U = S + J + Q - 2(E - D)$. $S =$ heat of sublimation of metal, $J =$ work of ionization of metal, $Q =$ heat of formation of chloride, $E =$ electron affinity of Cl, and $D =$ heat of dissociation of $\frac{1}{2}Cl_2$. $(E - D)$ and S_{Mn} from Grimm and Herzfeld (*loc. cit.*), J_{Mn} and J_{Fe} from Russell, Astrophys. Journ. lxvi. p. 233 (1927). S_{Fe} estimated at 100 using S_{Mn} and assuming proportionality with boiling-point. Other data from Landolt-Börnstein.

the force constants are obtained in the usual way from those given by Lennard-Jones (*loc. cit.*), and the coordination number is found to be 6, as observed, in all three cases.

The agreement is very good, deceptively so in the case of Zn^{2+}.

3. *The Energies of Coordination of Hydrates.*

A comparison on the same lines as the above is unfortunately impossible, as data are not available. Moreover, it is unjustifiable to draw any quantitative conclusions from a comparison of the values for hydrates and ammoniates of the same ion, for reasons given in II. If it could be assumed that an ion exists in solution as a hydrate having a definite known coordination number, and if certain other assumptions were made, a value for the energy of coordination could be obtained through the known heat of hydration of the ion. To do this it would be necessary to consider the introduction of the complex hydrato-ion into the solution unchanged. This would involve an energy change which may be described as the heat of hydration of the complex ion. Now Born * has given an expression for the heat of hydration of an ion in which the water is treated as a homogeneous dielectric and the absence of "chemical" hydration is assumed. If this expression could be applied to a complex ion all the necessary data would be obtained for calculating a value of the energy of coordination. We should have $-\phi = W - W_0 + 10n$, where W_0 is the heat of hydration of the complex ion and is obtained by substituting $r + 1\cdot3$ (where r is the equilibrium distance as in I., and $1\cdot3$ the kinetic theory radius of a water molecule) for r_i in Born's expression $W = 164z^2/r_i$, and where W is the heat of hydration of the simple ion (known) and $10n$ the heat of evaporation of $n\,H_2O$.

Calculation on these lines, assuming for lack of more definite information that the ions are hydrated to the extent indicated by the coordination numbers obtained in I., gives values of the energy of coordination for divalent ions which are higher by from 10 to 25 per cent. than the theoretical numbers. (The univalent ions are excluded from the calculation, as they are fairly certainly much less heavily hydrated.) These considerations are given as illustrating a possible line of attack, but no significance can be attached to the results, as both the procedure and the underlying assumptions are very doubtful.

* Born, *Z. Physik*, i. p. 45 (1920).

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LXIII. *The Production of Residual Double Refraction by Pressure in certain Glasses at Atmospheric Temperature. By* F. C. HARRIS, *M.Sc., University College, London* [*].

SOME years ago, in the course of an investigation into the effect of temperature on the stress-optical coefficients of various glasses, residual double refraction was produced in glass by applying pressure to the glass when heated to near the softening point, and allowing the glass to cool under this pressure [†]. On examining the glass so treated, some four years later, it was found that the residual double refraction had considerably decreased, and, in fact, in one case (that of an extra dense flint glass) had completely disappeared. Hitherto it has always been assumed that under ordinary atmospheric temperatures glass, of whatever chemical composition, exhibits no "optical creep" when subjected to uniform stress, the double refraction acquiring its maximum value immediately the stress is applied, and instantaneously returning to zero value on removal of the stress. In the case of cooling under pressure referred to above the residual double refraction was not uniform, but the fact that it considerably decreased during a long period under ordinary atmospheric temperatures indicated the possibility of producing residual double refraction, under atmospheric conditions, in glass by subjecting it to large pressures for a long time.

Three glasses were chosen having widely different percentage amounts of PbO, as it was thought that should any residual double refraction be produced its magnitude might conceivably be affected by the composition of the glass.

The glasses were :—

Percentage of PbO.

O. 152, containing SiO_2, PbO, K_2O, Na_2O............16

O. 103,   ,, SiO_2, PbO, K_2O...................47

S. 57,   ,, SiO_2, PbO..........................79

The first two glasses had positive stress-optical coefficients, and the third a negative coefficient.

A small straining frame was made in which the pressure was applied by means of screws. Each glass was placed in the frame and supported between knife-edge blocks. After

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[*] Communicated by Prof. L. N. G. Filon, D.Sc., F.R.S.
[†] Filon and Harris, Proc. Roy. Soc. A, ciii. p. 561.

careful "centreing," to obtain uniform stress in the central portion of each glass, pressure was applied and observations made in "sodium light" by a Babinet compensator in the usual way from time to time during the next three years.

Observations were made as follows :—

Date.	Glass.	Observations.	Adjustments.
5.1.28	O. 152 O. 103 S. 57	——	All subjected to pressures sufficient to produce 1 λ retardation in sodium light.
11.1.28	O. 152 O. 103 S. 57	Retardation just less than 1 λ. Retardation just less than 1 λ. No change observed.	All readjusted to show 1 λ retardation.
23.4.28	O. 152 O. 103 S. 57	No change observed.	
27.8.28	O. 152 O. 103 S. 57	Extremely small decrease in retardation.	All readjusted to show 1 λ retardation.
19.4.29	O. 152 O. 103 S. 57	No change observed.	
26.4.29	O. 152 O. 103 S. 57	Immediate return to zero retardation. Slight residual retardation. Definite residual retardation.	Pressure removed and glasses examined.
26.4.29	O. 152 O. 103 S. 57	——	Pressure applied sufficient to produce 1 λ retardation.
30.5.29	O. 152 O. 103 S. 57	No change observed.	
9.9.30	O. 152 O. 103 S. 57	No change observed.	
9.9.30	O. 152 O. 103 S. 57	Immediate return to zero retardation. 0·0356 λ residual retardation. 0·0462 λ residual retardation.	Pressure removed and glasses examined.

The two glasses O. 152 and O. 103 had been used some years previously by Filon and Jessop [*] in a series of experiments in which these glasses had been subjected to pressures sufficient to produce a retardation of 3 λ, and the load left on for 24 hours in the case of O. 152 and for 67 hours in the case of O. 103. It was observed that " in neither case was there any increase in the observed retardation during the time the load was left on, nor was there any trace of residual retardation on removal of the load." It was also stated that " had there been any creep, or a residual retardation *as great as* 0·01 λ, it must have been observed."

In the present case, from the above results, the residual retardation is *considerably greater than* 0·01 λ in the two

* Filon and Jessop, Phil. Trans. Roy. Soc. A, ccxxiii. p. 92.

glasses O. 103 and S. 57, and hence, in these two at any rate a definite residual double refraction has been produced. There was, however, no observable increase in the retardation during the time the load remained on.

Careful measurements were made of the dimensions of the glasses before and after loading, and any change that may have occurred was too small to measure.

The glasses were again examined one month later (*i.e.*, after the removal of the load), and it was found that all trace of the residual double refraction had disappeared. In view of this surprisingly rapid decrease in the residual retardation, glasses S. 57 and O. 103, and also later another glass, 4840 (which had been used in the production of residual retardation by cooling under pressure, mentioned at the beginning of this note), were again subjected to uniform pressure as before, with the following results :—

Date.	Glass.	Observations.	Adjustments.
17.10.30	O. 103 / S. 57	——	Subjected to uniform pressures producing a retardation of 2 λ.
20.10.30	O. 103 / S. 57	Slight decrease in retardation.	Both readjusted to show a retardation of 2 λ.
22.10.30 to 3.11.30	O. 103 / S. 57	No change.	
3.11.30	O. 103 / S. 57	Immediate return to zero. Residual retardation = 0·042 λ.	Unloaded.
4.11.30	S. 57	,, ,, = 0·042 λ.	
5.11.30	S. 57	,, ,, = 0·038 λ.	
6.11.30	S. 57	,, ,, = 0·028 λ.	
12.11.30	S. 57	,, ,, = 0·022 λ.	
17.11.30	O. 103 / S. 57 / 4840	——	Subjected to uniform pressures producing a retardation of 2 λ.
18.11.30	O. 103 / S. 57 / 4840	Slight decrease in retardation.	All readjusted to show a retardation of 2 λ.

The pressures were maintained till 15.12.30 and then removed, the following observations being made :—

Date.	Glass.	Observations.	
15.12.30	O. 103	Immediate return to zero.	
	S. 57	Residual retardation = 0·063 λ.	
	4840	Very slight residual retardation.	Too small to measure.
16.12.30	S. 57	Residual retardation = 0·054 λ.	
17.12.30	S. 57	,, ,, = 0·037 λ.	
18.12.30	S. 57	,, ,, = 0·034 λ.	
19.12.30	S. 57	,, ,, = 0·034 λ.	
30.12.30	S. 57	,, ,, = 0·019 λ.	
5. 1.31	S. 57	Residual retardation too small to measure.	

The composition of glass 4840 was :—SiO_2 30·4 per cent. ; PbO 64·4 per cent. ; and small amounts of Al_2O_3, K_2O, CaO, As_2O_5.

The above results show that a definite residual retardation is produced in certain glasses at atmospheric temperature by applying uniform pressure for a long period ; also for simple glasses containing large amounts of PbO the residual double refraction is produced in a less time than for glasses containing smaller amounts of PbO, or, alternatively, in any given time the magnitude of the residual double refraction is greater for glasses containing large amounts of PbO than for those containing small amounts. Although 4840 contained a comparatively large amount of PbO (64·4 per cent.), the presence of so many other constituents seems to counteract the effect of the PbO.

In no case was there any observed increase in the double refraction during the time the load was left on.

LXIV. *The Insulation of Pyrex Glass after Heating* in vacuo. *By* J. H. MITCHELL, *H. H. Wills' Physical Laboratory, University of Bristol* *.

IT had been noticed in this laboratory that pyrex glass loses permanently much of its electrical insulating property after baking out in a vacuum. Initially it is a sufficiently good insulator for use with an electrometer, but after the usual heat treatment given to vacuum apparatus the insulation becomes spoiled to a certain extent. It appeared of value to investigate this behaviour more closely.

The apparatus, fig. 1, to make observations on this consisted of a pyrex tube joined by a T-piece to a vacuum apparatus, and closed at its ends by pyrex stoppers (i and ii). Pyrex tubing of 1 cm. diameter was joined to stopper ii, and was platinized at *a* in order to make electrical contact, leaving a break in the platinizing of about 1 cm. in length at *f*. The platinizing formed two separate contacts with the glass ; the first was connected by the lead *d* to a steady potential which could be used at any required value, and the second by the lead *c* to a

quadrant electrometer. The stopper i carried a furnace
b, so that when the apparatus was assembled the portion
f was at the middle of the furnace. Thus the resistance
of *f* could be determined under varying conditions, the
temperature variations being measured by a calibrated
thermo-couple inserted in stopper ii with the junction at
the centre of *f*. Contact potentials were balanced out by

Fig. 1.
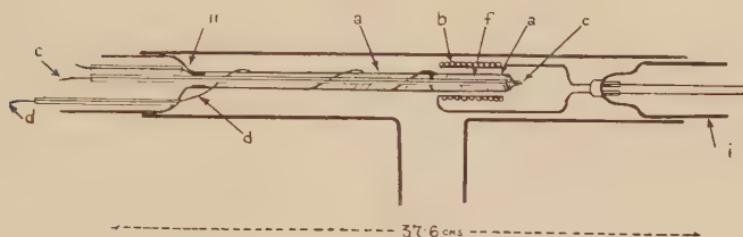
Fig. 2.
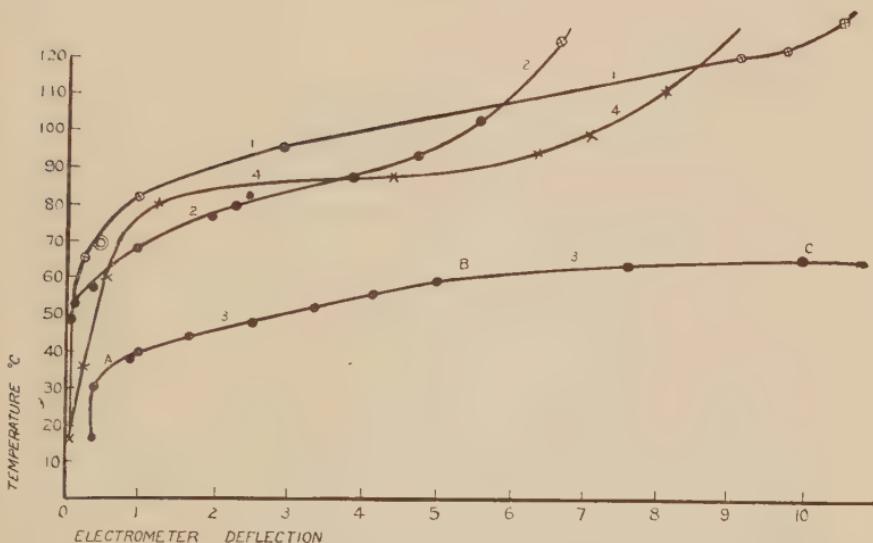
means of a potentiometer or by the determination of the
potential and subsequent subtraction.

Specimens were heated *in vacuo*, and were tested for
increase in conductivity with rise in temperature. Typical
curves are those of fig. 2. Curves 1 and 2 were taken
over a wide range of temperatures, and show the general
form of the observed curves. They show a rapid increase
in conductivity between the temperatures of 55° C. and

80° C., varying slightly for different specimens. For curves 1, 2, and 4 there was a potential drop of 2 volts across the specimen. In curve 3 a potential drop of 30 volts was used, and the curve suggests that the increase in conductivity takes place in steps, the first OA, the second AB, and then a rapid increase BC. The point B gives the position where the increase in conductivity is most noticeable. The cooling curves, of which 4 is an example, show a great similarity to the heating curves. The curves 1 and 2 show for higher temperatures a tendency to approach a constant limiting conductivity. The points at this end of the curve are not reliable, due to the difficulty of accurate measurement of a rapid rate of deflexion of the electrometer.

The heating was continued to higher temperatures ; the method was to heat the glass at a steady temperature for 30 minutes and allow to cool for about 16 hours, the conductivity being noted before and after heating. The heating was then repeated at higher temperatures. In this way it was found that (1) after heating to a tempera- ture of 250–300° C. a decrease in conductivity of the glass was produced, and (2) after heating at temperatures of 350–400° C. there was a very marked increase in con- ductivity. The first effect, shown in columns C and D of the table, is probably simply the result of a thorough drying of the glass, and the resultant conductivity is probably the true conductivity of the glass. The second is a permanent increase, and all specimens showed the same characteristics although there were considerable variations of detail. This permanent increase will be denoted by the " break-down " conductivity of the specimen. Columns A and B of the table give the temperatures at which this " break-down " was produced. Specimens 1–5 and 6–8 were from two different stocks of pyrex. Pressure changes showed no alteration of the effect providing the pressure in each case was below 1/10 mm. mercury. Specimen 3 showed no change in conductivity when heated in air at atmospheric pressure, although the heating was continued to a temperature of 650° C. ; neither was the effect ob- served by heating in hydrogen at a few mm. pressure. The mean initial resistance of a strip 1 cm. by 1 cm. was of the order of 10^{13} ohms. The ratio column (α) of the table gives the number of times the conductivity has been increased by this effect, the mean ratio being 23.

The following methods were used in attempts to restore the " broken-down " specimens to their former low conductivity :—

    (1) Allowing the specimen to stand in air.
    (2) Immersion in liquid air.
    (3) Treatment with hydrofluoric acid.
    (4) Heating at atmospheric pressure in air.

No.	Temperature of breakdown.		Rate of electrometer deflexion.					Ratio.		
	Small.	Marked.	Original.	After heating at 260° C.	After cooling.		After 4½ hrs. heating in air.	α.	β.	γ.
					16 hrs.	100 hrs.				
	A.	B.	C.	D.	E.	F.	G.	F./D.	G./D.	α./β.
1	°C. 360	°C. 420	·10	·07	4·7	2·4	-	34·3	—	—
2	345	400	·18	·14	5·1	2·9	—	21	—	—
3	to 6,60° C.		Heated in air. — No breakdown.			—		- -	—	—
4	380	420	·28	·18	9·1	3·1	—	17	—	—
5	350	400	·12	·06	6·2	2·95	·30	49	5	10
6	400	500	·399	·216	1·612	1·401	·62	6·5	2·8	2·3
7	390	450	·61	·34	3·83	,3·65	·61	10·7	1·8	6·0
8	370	450	·53	·50	6·8	—	—	—	—	—

(1) It was found that there was a steady decrease in conductivity whilst the specimen was cooling. Fig. 3 and columns E and F of the table show this decrease during the first 100 hours after the heating causing the " break-down " had been removed and the specimen had returned to room-temperature (18° C.). Over long intervals of time specimens decreased in conductivity to a small extent, the rate of decrease eventually becoming negligibly small. Thus

specimen 1 decreased in conductivity from a rate of electrometer deflexion of 4·7 to one of 2·4 in 100 hours : the decrease during the next two months, however, was only to one of 1·91, and no further decrease was found.

(2) Specimens 1 and 2 were left in liquid air for about 40 hours, but no decrease in their conductivity was found.

(3) The surface layer of glass of specimens 1, 2, 4, and 8 was removed by a wash of hydrofluoric acid. A nearly complete restoration to former conductivity was found. Thus specimen 1, whose original rate of electrometer deflexion was 0·10, upon being " broken-down " for 100 hours had a rate of 1·91. A wash of hydrofluoric acid restored the specimen to a rate of 0·206. Specimens 2 and 4 were similarly treated. They had original rates of electrometer deflexions of 0·18 and 0·28 ; after being " broken-down " 100 hours the rates were 2·9 and 3·1, and after a hydrofluoric acid wash the rates were 0·225 and 0·32 respectively. Thus these show an almost complete restoration. Specimen 8, which had been " broken-down" only 16 hours, appeared completely restored by the treatment. Its original rate of deflexion was 0·53, after being " broken-down " 16 hours 6·8, and after the wash of acid 0·54, showing a complete restoration.

(4) Specimens 5, 6, and 7 were heated in air at atmospheric pressure at a temperature of about 500° C. for 30 minutes. A decrease in conductivity was found which continued on resuming the heating until the specimen was much restored, but no complete restoration was obtained, although the heating was continued for many hours. The specimens were now heated *in vacuo*, to obtain the " break-down " a second time. It was found, however, that they could not be further " broken-down" even when heated at 550° C. for several hours. A comparison of columns C, D, F, and G of the table gives an idea of the order of this improvement. The ratio column " β " shows the number of times the remaining conductivity is greater than the original, and it is noticeable that the order is still quite large. The ratio column γ clearly shows the order of the decrease in conductivity due to heating in air.

It was noticed that after heating in vacuum th_ specimens lost a little of their transparency and became _ htly cloudy. Observations under the microscope showed the cloudiness to be due to bubbles. The bubbles were also

present in specimens 5, 6, and 7 after their long period of heating. A specimen full of these bubbles was made by heating pyrex in an oxygen blowpipe flame, its resistance measured, and found to be of the same order as that of specimens 1 and 2. It seems probable that these bubbles are caused by gas being driven off from the glass, and have little or no effect upon its insulation and conductivity.

The fact that a wash with hydrofluoric acid restores the conductivity shows that the permanent increase in conductivity of a specimen after vacuum heating is a surface effect. It is probably due to some chemical change in the outer layers of the glass, connected with the gas evolution which occurs under these conditions. From a practical point of view the results are of importance in vacuum technique in showing to what extent pyrex glass is satisfactory as an insulator.

In practice we find that though pieces of tube about 5 cm. in length can be used perfectly satisfactorily for electrometer insulation, small beads are apt to give trouble.

In conclusion, I should like to thank Dr. H. W. B. Skinner for suggesting this problem and for technical assistance.

LXV. *On the Reduction of Dynamics to Geometry.* *By* T. Lewis, *University College of Wales, Aberystwyth* [*].

Introduction.

HERTZ, in his book 'The Principles of Mechanics,' has shown that the study of the dynamics of a *free* system with n degrees of freedom can be reduced to the study of geodesics in a certain n-dimensional space. For example : " § 347. *Proposition.* The natural path of a free holonomous system between any two sufficiently near positions is shorter than any other possible path between the two positions." Or, again : " § 352. *Proposition.* The natural motion of a free holonomous system carries the system in a shorter time from a given initial position to a sufficiently near one, than could be done with any other possible motion, with the same constant value of the energy."

By a "*free*" system Hertz meant a system free from the action of external forces. The idea of a system acted upon by external forces is introduced by dividing a *free* system into two (or more) partial, *coupled* systems. The above propositions are not true for one of these partial systems—the equations giving geodesics have to be supplemented by terms representing the effect of the coupling, or, in the ordinary language of mechanics, the external forces.

Synge[*] has also studied dynamical systems from this point of view, using the notation and methods of the Tensor Calculus. He considers two line elements associated with the "manifold of configurations" and the corresponding geodesics (or trajectories) in the spaces characterized by these line elements, namely, the *kinematical line element*

$$ds^2 = 2\mathrm{T}\,dt^2,$$

and the *action line element*

$$ds^2 = 2(h - \mathrm{V})\mathrm{T}\,dt^2.$$

However, both these authors consider the paths of a dynamical system in ordinary n-dimensional space, where n is the number of degrees of freedom of the system. This involves two disadvantages. Firstly, in the kinematical space the trajectories are geodesics only when external forces are absent or when certain conditions are satisfied by the force potential. Secondly, the *action line element* is a function of the total energy h, so that only trajectories having the same total energy can be compared.

The "General Theory of Relativity," on the other hand, has taught us the advantages gained by considering the nature of the path described by the dynamical system in an $(n+1)$-dimensional space, the additional dimension being different in kind from the others—it is said to be time-like. But, so far, this method has not been applied to strictly Newtonian systems. It is true that Synge suggests that interesting results might repay the study of the line elements

$$ds^2 = 2\mathrm{L}\,dt^2 \quad \text{and} \quad ds = 2\mathrm{L}\,dt,$$

but he has confined himself to the study of the first two. In what follows we shall prove that Hertz's propositions are true, word for word, for *any* conservative holonomous system, referred to a certain $(n+1)$-dimensional space instead of the n-dimensional space imagined by Hertz.

[*] J. L. Synge, "On the Geometry of Dynamics," Phil. Trans. A, p. 226 (1926).

The line element in this $(n+1)$ space is slightly different from the one suggested by Synge, and the extra dimension must not be interpreted as the time in the Newtonian sense. Newtonian time appears as a mere parameter, which is really determined by the motion of the system in this $(n+1)$ space, and it needs no further definition. The extra dimension is that into which ordinary space "unfolds" itself, or into which it "grows," and the rate of growth at any point depends upon the Newtonian potential.

The appropriate forms of the canonical equations and the Hamilton-Jacobi differential equation will be deduced, and, finally, Schrödinger's wave equation. Some extensions and simple applications are suggested.

§ 1. *A Line-element characteristic of Newtonian Dynamics.*

Let us consider a line-element of the form

$$ds^2 = \frac{du^2}{\phi} + \alpha_{ij} \, dq_i \, dq_j, \quad \cdots \quad (1.1)$$

where ϕ and α_{ij} are functions of the q_r only, and summation is carried out whenever a suffix occurs twice.

The geodesics corresponding to this line-element are defined by the variational equation

$$\delta \int_A^P ds = 0.$$

Introducing a parameter τ, and denoting differentiation with respect to it by dots, this equation becomes

$$\left[\dot{s} \, \delta \tau \right]_A^P + \int_{\tau_0}^\tau \delta \sqrt{\frac{\dot{u}^2}{\phi} + \alpha_{ij} \dot{q}_i \dot{q}_j} \, d\tau = 0.$$

The variations δq_i vanish at the extremities and τ can always be chosen such that $\delta \tau = 0$ at A and P. Proceeding in the usual way, we arrive at the differential equations of the geodesic, namely,

$$\frac{du}{ds} = K\phi, \quad (K = \text{constant}) \quad (1.2)$$

$$\frac{d}{ds} \left(\alpha_{ij} \frac{dq_j}{ds} \right) + \frac{1}{2\phi^2} \left(\frac{du}{ds} \right)^2 \frac{\partial \phi}{\partial q_i} - \frac{1}{2} \frac{\partial \alpha_{jk}}{\partial q_i} \frac{dq_j}{ds} \cdot \frac{dq_k}{ds} = 0. \quad (1.3)$$

If now we write

$$K = \pm \sqrt{2}, \quad \cdots \quad (1.4)$$

equations (1.3) become

$$\frac{d}{ds}(\alpha_{ij}\dot{q}_j) + \frac{\partial\phi}{\partial q_i} - \frac{1}{2}\frac{\partial\alpha_{jk}}{\partial q_i}\dot{q}_j\dot{q}_k = 0, \quad . \quad . \quad . \quad (1.5)$$

where dots now denote differentiation with respect to s.

Again, writing

$$\mathrm{T} = \tfrac{1}{2}\alpha_{ij}\dot{q}_i\dot{q}_j, \quad \mathrm{L} = \mathrm{T} - \phi, \quad . \quad . \quad (1.6)$$

equations (1.5) can be put in the form

$$\frac{d}{ds}\cdot\frac{\partial\mathrm{L}}{\partial\dot{q}_i} - \frac{\partial\mathrm{L}}{\partial\dot{q}_i} = 0,$$

i. e., they are the equations of motion of a conservative holonomous system having n degrees of freedom, s being the Newtonian time, T the usual kinetic energy, and ϕ the potential energy.

The integral of energy for this system follows at once. It is

$$\mathrm{T} + \phi = \tfrac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad (1.7)$$

The total energy is completely determined, because the unit of time which we have adopted is the natural unit, defined by the motion of the system itself and without reference to any external time keeper. However, we can always adopt an arbitrary unit of time. We notice that (1.3) is homogeneous and of degree -2 in ds. Hence if we write

$$s = \pm \sqrt{2h}\,\tau \quad . \quad . \quad . \quad . \quad . \quad (1.8)$$

it remains invariant. But instead of (1.4) we must now write

$$\mathrm{K} = \pm 2\sqrt{h}, \quad . \quad . \quad . \quad . \quad (1.4')$$

in order that (1.5) may be invariant.

The integral of energy now becomes

$$\mathrm{T} + \phi = h. \quad . \quad . \quad . \quad . \quad . \quad (1.7')$$

Since it is usual to adopt an arbitrary unit of time in the study of dynamical problems, we shall in future regard τ as the time and s as the *natural* or *proper* time of the system.

We have thus proved the following proposition :—*A holonomous system, with* n *degrees of freedom, moving in a conservative field of force, may be treated as a free system with* (n + 1) *degrees of freedom, the coordinate corresponding to the extra degree of freedom introduced being ignorable. The path of the system in this* (n + 1) *space is a geodesic described with constant speed* $\sqrt{2h}$ (*cf.* Hertz, § 410, (ii)).

§ 2. *Hamilton's Canonical Form for the Equations of a Geodesic.*

Let us write

$$\mathrm{H} = \frac{1}{2}\left(\frac{\dot{u}^2}{\phi} + \alpha_i \dot{q}_i \dot{q}_j\right); \quad \ldots \quad (2.1)$$

$\dot{u}$, $\dot{q}_i$ are to be regarded as the contravariant components of a vector. The corresponding covariant components are defined by the equations

$$v = \frac{\partial \mathrm{H}}{\partial \dot{u}} = \frac{\dot{u}}{\phi}, \qquad p_i = \frac{\partial \mathrm{H}}{\partial \dot{q}_i} = \alpha_{ij} \dot{q}_j. \quad \ldots \quad (2.2)$$

The contravariant components can be expressed in terms of the covariant components thus :

$$\dot{u} = v\phi, \qquad \dot{q}_i = \alpha^{ij} p_j, \quad \ldots \quad (2.3)$$

where α^{ij} is the cofactor of α_{ij} in the determinant $|\alpha_{ij}|$ divided by this determinant.

H can be expressed in the following ways :—

$$\mathrm{H}(u, v, q, p) \equiv \tfrac{1}{2}(v^2 \phi + \alpha^{ij} p_i p_j), \quad \ldots \quad (2.4)$$

$$\mathrm{H}(\dot{u}, v, \dot{q}, p) \equiv \tfrac{1}{2}(v\dot{u} + p_i \dot{q}_i). \quad \ldots \quad (2.5)$$

If we consider the form (2.4) we can easily verify that the equations of a geodesic can be expressed in canonical form thus :—

$$\left. \begin{aligned} \dot{u} &= \frac{\partial \mathrm{H}}{\partial v}, & v &= -\frac{\partial \mathrm{H}}{\partial u} \equiv 0, \\ \dot{q}_i &= \frac{\partial \mathrm{H}}{\partial p_i}, & \dot{p}_i &= -\frac{\partial \mathrm{H}}{\partial \dot{q}_i}. \end{aligned} \right\} \quad \ldots \quad (2.6)$$

The equation of energy is

$$\mathrm{H} = h. \quad \ldots \quad \ldots \quad (2.7)$$

§ 3. *The Hamilton-Jacobi Differential Equation.*

In a transformation of coordinates the covariant components of a vector behave in the same way as the components of the gradient of a scalar. It is therefore natural to look for a solution of our dynamical (or geometrical) problem in which (v, p_i) are proportional to the components of the gradient of a certain scalar.

Let us try

$$v = \frac{\partial \mathrm{S}}{\partial u}, \qquad p_i = \frac{\partial \mathrm{S}}{\partial q_i}. \quad \ldots \quad (3.1)$$

Substituting these expressions in the equation of energy,

$$H(u, v, q, p) = h,$$

we get the appropriate form of the Hamilton-Jacobi partial differential equation, namely,

$$\phi\left(\frac{\partial S}{\partial u}\right)^2 + a^{ij}\frac{\partial S}{\partial q_i}\frac{\partial S}{\partial q_j} - 2h = 0. \quad . \quad . \quad . \quad (3.2)$$

But ϕ and α^i are independent of u; so we may obtain a solution of (3.1) by separation of variables.

Let

$$S = U + V, \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

where U is a function of u only and V is independent of u.

Substituting for S in (3.1) we find that

$$\left(\frac{dU}{du}\right)^2 = a^2 = \left(2h - \alpha^{ij}\frac{\partial V}{\partial q_i}\frac{\partial V}{\partial q_j}\right)\Big/\phi.$$

Making a^2 equal to 2, these equations become

$$\left.\begin{aligned}
U &= \pm \sqrt{2}\,u, \\
\alpha^{ij}\frac{\partial V}{\partial q_i} \cdot \frac{\partial V}{\partial q_j} - 2(h - \dot{\phi}) &= 0.
\end{aligned}\right\} \quad . \quad . \quad . \quad (3.4)$$

The second of these equations is the Hamilton-Jacobi equation of Newtonian dynamics, and it is known that a complete solution leads to the solution of the dynamical problem.

§ 4. *Transition to Wave Mechanics.*

If we wish to investigate physical phenomena on a microscopic scale particle mechanics is replaced by wave mechanics. Equation (3.2) is now replaced by a wave equation of the second order. Various methods of bridging the gap between the two types of mechanics have been suggested. Here, instead of assuming

$$H\left(u, \frac{\partial S}{\partial u}, q, \frac{\partial S}{\partial q}\right)$$

to be constant, we assume that its integral taken throughout a region of the $(n+1)$ space is stationary, subject to S being prescribed on the boundary and to the condition

$$\int S^2 d\Omega = \text{constant.}$$

The element of volume is defined by the equation

$$d\Omega = \sqrt{\Delta}\, du\, dq_1 \ldots dq_n,$$

where

$$\Delta = |\alpha_{ij}|\, \phi^{-1}.$$

The wave equation is the condition that

$$\delta \int_\Omega \left\{ \phi \left(\frac{\partial S}{\partial u} \right)^2 + \alpha^{ij} \frac{\partial S}{\partial q_i} \cdot \frac{\partial S}{\partial q_j} \right\} \sqrt{\Delta}\, du\, dq = 0, \quad (4.1)$$

subject to

$$\delta \int_\Omega S^2 \sqrt{\Delta}\, du\, dq = 0 \quad \ldots \quad (4.2)$$

and the vanishing of δS on the boundary of Ω.

Variation and partial integration lead to the equation

$$\frac{\partial}{\partial q_i} \left(\alpha^{ij} \sqrt{\Delta} \frac{\partial S}{\partial q_j} \right) + \phi \sqrt{\Delta} \frac{\partial^2 S}{\partial u^2} + \mu \sqrt{\Delta} S = 0, \quad (4.3)$$

μ being a constant.

For periodic phenomena the solution of (4.3) will be of the form

$$S = \psi / e^{i\nu u}, \quad \ldots \quad \ldots \quad (4.4)$$

where ν is the frequency, and ψ is the amplitude, satisfying the equation

$$\frac{\partial}{\partial q_i} \left(\alpha^{ij} \sqrt{\Delta} \frac{\partial \psi}{\partial q_j} \right) + \nu^2 \sqrt{\Delta} (h - \phi) \psi = 0, \quad . \quad (4.5)$$

with $h = \mu / \nu^2$.

This last equation is identical with Schrödinger's amplitude equation. The only solutions admitted by Schrödinger and his school are those which are one-valued and free from singularities. These conditions, in general, lead to a series of characteristic values of the constant h. In this connexion a point of some interest suggests itself. Schrödinger found that in the case of hydrogen-like atoms there are no positive characteristic values of h. The manner in which we have derived the amplitude equation (4.5) leads us to expect this result; for a positive value of h does not correspond to a periodic motion of the electron, but to a parabolic or hyperbolic motion, and we are not justified in making the assumption (4.4) with ν real. Hence in such a case the amplitude does not satisfy (4.5), but an analogous equation with $-\nu^2$ instead of ν^2. A glance at Schrödinger's [*] mathematical

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[*] E. Schrödinger, *Ann. d. Phys.* lxxix. (1926).

analysis of the problem shows that the characteristic values
of h with reference to this modified equation are positive and
equal in absolute magnitude to those occurring in the original
problem.   It is possible that systems of this type contribute
as much to spectral lines as periodic systems do.

§ 5. *Remarks and Applications.*

Usually Newtonian dynamics is regarded as a first
approximation to relativity dynamics.   But the above
analysis shows that Newtonian and relativity dynamics are
both special cases of the geometry of a kinematical $(n+1)$
space.   There is no reason why the Principle of Equivalence
of acceleration and gravitation should not be combined with
Newton's gravitational law—the law of inverse square.   On
the basis of these two postulates it is found that a light ray
(or, if preferred, a light quantum) on grazing a massive
gravitating body undergoes a deflexion of amount equal to
that found by Einstein on the basis of Fermat's and
Huygen's Principles, *i. e.*, one-half of the deflexion calcu-
lated on the basis of the *General Theory of Relativity*.   The
shift of the spectral lines also is one-half of that predicted
by the *General Theory of Relativity*.   In these examples the
line element has the form

$$ds^2 = -\frac{du^2}{1+\dfrac{m}{r}} + dr^2 + r^2(d\theta^2 + \sin^2\theta \, d\psi^2),$$

where m is the mass of the gravitating body and r is
measured from its centre.   At infinity it reduces to the line
element of the *Special Theory of Relativity*.

There is no difficulty in extending the above analysis so
as to include non-holonomous systems in which the equa-
tions of constraint do not depend explicitly upon u.   In this
case the path of the system is not a geodesic, but its length
is stationary as compared with neighbouring paths which
are consistent with the equations of constraint.

I have to thank Prof. Schott for his criticism and
advice.

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LXVI. *New Bands in the Secondary Spectrum of Hydrogen.*
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THE Secondary Spectrum of Hydrogen has been the
subject of investigations, both experimental and
theoretical, for a long time. A very valuable help to the
theoretical work in the subject has been rendered by the
extremely accurate experimental data supplied by some
recent investigators. The works of Finkelnburg [1] and of
Gale, Monk, and Lee [2], stand very conspicuously amongst
others (Merton and Barratt, Tanaka, Deodhar, Porlezza,
Watson, Sandemann, Allibone, and others). Finkelnburg
has given a list of 3667 lines between λ 4861 and λ 3314,
with accuracy of wave-length measurements to the third
place of decimals. Gale, Monk, and Lee's list of wave-
lengths gives measurements of 3064 lines between λ 8092
and λ 3394, out of which wave-lengths up to λ 7000 are
accurate up to two, and those below (to λ 3394) to three
decimal places. Of course in the regions common to both
lists there are many common lines. In fact Finkelnburg's
list includes, besides his own measurements, lines in that
region measured by Gale, Monk, and Lee, Merton and
Barratt, Deodhar, Tanaka, Porlezza, and Watson. All these
experimental data, with their very high accuracy, have indeed
afforded great facility to the theoretical investigators in
their attempts at classification and explanation of the
spectrum.

In a recent discussion on molecular spectra held under
the auspices of the Faraday Society, Prof. O. W. Richardson
has given a comprehensive account of spectral classification
of the lines in the secondary spectrum of hydrogen
(a summary account of which he has also given in his latest
paper, Proc. Roy. Soc. cxxvi. p. 487) as regards their
electronic transitions in the molecule. From a study of
this paper and the others (referred to therein), which give
the detailed vibrational and rotational classifications of the
lines, it appears that the origin of more than 80 per cent.
of the lines is still unknown. Even amongst the bands
whose vibration and rotation structures are known there
are many for which it has not been found possible to assign
the exact electronic levels. It is quite evident therefore

that a large number of bands and electronic levels remain to be discovered. A careful study of the analysis hitherto effected shows clearly that band systems so far discovered all satisfy the usual rules of selection principles for electronic transitions, viz., only the transitions

$$\Delta k = \pm 1, \ \Delta j = 0, \ \pm 1 \text{ and } \Delta s = 0 \text{ are allowed}$$

(where ' s ' is the spin quantum number, 0, $\frac{1}{2}$, 1,... for singlets, doublets, triplets,.........).

These selection rules, initially discovered and found applicable almost without exception in the case of atomic spectra under normal conditions, have been found to be violated under different abnormal conditions. It is well known that in the case of atoms the selection rules $\Delta k = \pm 1$ and $\Delta s = 0$ are readily violated in presence of strong electrostatic fields. For example, Koch [3] obtained in a strong electrostatic field the $2p - mp$ lines of helium, and found that the intensity varies proportionally to the field strength. Recently Nils Ryde [4] obtained the forbidden lines ($p - f$, $p - g$ combinations) of neon by a similar arrangement. The violation of the other selection rule, $\Delta s = 0$, is very common, and is exhibited in the intercombination lines obtained in atomic spectra. The intercombination lines are readily obtained in heavy current arcs, as was shown by Dr. Sur [5] in the case of lead in this laboratory. The present author [6] also got the fundamental intercombination lines of carbon in the heavy arc of carbon. Recently Paschen [7] announces the discovery of the $^1S - {}^3P$ line of helium in a heavy current discharge through helium. In the case of molecules, therefore, it may quite reasonably be expected that these selection rules ($\Delta k = \pm 1, \Delta s = 0$) may be very readily violated, for in the formation of molecules out of atoms the electrons are subjected to intense electrostatic fields, and therefore it is expected that such usually forbidden transitions as $\Delta K = \pm 0$; $2 \ldots \Delta s = \pm 1$ may possibly be obtained more readily in molecular spectra.

Proceeding on this idea, I have tried to find out whether lines can be selected corresponding to the electronic transition $\Delta k = 0$ from the hitherto discovered electron levels of hydrogen molecule. In this paper in the first section is given a summary of the information of the known electronic levels of hydrogen. This has been mainly prepared from the above-mentioned report of Richardson, supplemented from the works of Dieke [8], Hori [9], Finkelnburg and Mecke [10], and others. An interpretation of the levels according to Hund's theory of axial quantization

has also been given. In the second section I have given
the results of my attempted identification of bands of the
forbidden transition $\Delta k = 0$ in the visible region. It is
quite important to mention that Richardson [11] has made
a passing reference* to the possibility of such transitions
by assigning his 3^1Q-level, which combines with $2p^1\Sigma$, giving
very weak progressions, as $3p^1\pi_{a,b}$, and therefore seems to
be in favour of this view. The particular transition that
I have chosen is between the B-level of Dieke and the 3^3P-
levels of Richardson; the vibration and rotation structures
of both of which are more or less completely known with
great definiteness and accuracy from the analysis of
Richardson and his co-workers [12, 13]. As the point as to
whether the 3^3P-level of Richardson (the initial level of the
α-bands) is a $^1\pi$ or $^3\pi$ level is not yet definitely decided, it
cannot be said just now if in this transition the selection
$\Delta s = 0$ is also simultaneously violated.

§ 1. *Electronic Levels of the Hydrogen Molecule.*

The following table, prepared mainly on the basis of the
report of Prof. O. W. Richardson, gives the energy values
and probable positions of the hitherto identified electron
levels of the hydrogen molecule (according to the recent
theories). It contains identifications done definitely as well
as provisionally. For the manner in which the term values
have been determined by Richardson reference may be
made to his original papers.

Before proceeding to explain the table, however, it may
be useful to summarize briefly the application of Hund's
theory of axial quantization, in calculating the electronic
terms for the molecule of hydrogen in particular. Heissen-
berg and Hund have pointed out that their theory for
calculating electron terms from electron configurations in
the case of atoms can be extended with some modifications
to the case of molecules also. The main features of their
theory for diatomic molecules are :—

(1) As in the case of molecules a strong electrostatic
field (due to the two nuclei) along the nuclear axis is
superposed on the central nuclear field, there should arise
sequences additional to the usual S, P, D... for atoms.

(2) In atoms each electron has an orbital angular
momentum, corresponding to the azimuthal quantum

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* I became acquainted with this suggestion after this paper was
written.

Table I.—Electronic Terms of Hydrogen (Molecule).

n	l=1	s — 0 (1)	s — 0 (3)	p — 1 (1)	p — 1 (3)	p — 1 (1)	p — 1 (3)	d — 2 (1)	d — 2 (3)	d — 2 (1)	d — 2 (3)	d — 2 (1)	d — 2 (3)
1		[A]1s¹Σ 124569 4262 —		[B]2p¹Σ 34872 1337·7 38·9	2p³Σ [48000]?	[C]2p¹Π 25475 2380 59	2p³Π 29500 — —						
2		2s¹Σ 25300 2350 50	2s³Σ (Infra Red.) 29338 2594 66·7										
3		3s¹Σ [30]? 11614 2414 59	3s³Σ [3¹K]? 12937 2290 21·8	3p¹Σ	3p³Σ 17733 2130 53·1	3p¹Π [3¹Q]?	3p³Π_{a,b} 12719 2307 59	[3¹C]3d¹Σ 12758 2340 ?	3d³Σ	[3¹A¹B]3d¹Π_{a,} 12546 2143 40?	3d³Π 12515 2175 40?	3d¹Δ_{a,b} [λ4097] upper 9935(?)	3d³Δ
4		4s¹Σ [4¹E]? 7187 — ab. 60	4s³Σ	4p¹Σ	4p³Σ 8810 2184 57	4p¹Π	4p³Π_{a,b} 7067 2276 58·8	[4¹C]4d¹Σ 7152·5 ab. 60	4d³Σ	[4¹A¹B]+d¹Π_{a,b} 7008 ab. 60	4d''1 6991 ca. 2000 ab. 60	[4¹X]4d¹Δ 6761 — ab. 60 [λ4143] upper 10000? 75	4d³Δ
5							5p³Π_{a,b} 4493 2251						
6							6p³Π_{a,b}						

Annotations on the chart:

[U. Violet] Werner Bands.
[U. Violet] Lyman Bands.
Infra Red.
[Visible α, β, γ, δ Bands (Richardson and Das).]

number k_e, and a half quantum number s_e, of the spin angular momentum. The resultant of all the k_e's and s_e's is denoted by l and s respectively. In the case of molecules this l may be supposed to execute, in ordinary cases, an essentially uniform precessional motion about the nuclear axis, because of the strong axial field, due to the two nuclei being superposed on the central field. The l of the electrons, therefore, being electrically coupled to the inter-nuclear axis, gets quantized about it and resolves into two components, one along this axis and the other perpendicular to it. (The latter component does not concern us here for the present.) The λ may have all integral values between l and 0.

Thus for

$$l = 0, \quad \lambda = 0,$$
$$l = 1, \quad \lambda = 0, 1,$$
$$l = 2, \quad \lambda = 0, 1, 2,$$

and so on.

(3) As in atomic spectra s is not affected directly by the electric field of the nuclei, but it (s) tends to react magnetically with l. Here λ (the component of l along the nuclear axis) is effective in orienting s (as l precesses rapidly about the nuclear axis).

(4) With given values of λ and s the same terms as in the case of atoms are obtained.

With this review of Hund's theory let us now proceed actually to calculate the electronic terms of the hydrogen molecule.

In the normal hydrogen molecule the electron in each atom is in the normal K_1-level (or $1s$-state). It is assumed that in the excited state of the molecule one of the two electrons continues to occupy its normal position (the K_1-level) in its atom, whereas only the other electron is excited, occupying the higher levels (L, M, N...) in the atom. Richardson states that there are spectroscopic evidences for this assumption. Taking this assumption to be justified, let us now calculate the electronic terms in the different states of excitation of the molecule. We shall designate the excited states of the molecule as K_1X_1, K_1X_2, K_1X_3, .. according as the running electron occupies the s (*i. e.*, the L_1, M_1, N_1,...) levels or the p (L_2, M_2, N_2,...) levels, or the d (M_3, N_3, O_3,...) levels...... respectively.

Calculation of Terms.

Normal state,

$$K_1K_1 \qquad l_1 = 0, \quad l_2 = 0,$$
$$\lambda_1 = 0, \quad \lambda_2 = 0,$$

resultant $\qquad \Lambda = 0 \quad \therefore \quad$ a Σ-state.

Extending Pauli's principle to the molecular case also :

$$s_1 = \pm\tfrac{1}{2}, \quad s_2 = \mp\tfrac{1}{2},$$
$$S = 0 \quad \therefore \quad \text{a singlet.}$$

The resulting term is $^1\Sigma$.

(In order to distinguish from the electronic terms S, P, D,... in atoms corresponding to $l = 0, 1, 2,...$ the molecular terms corresponding to $\Lambda = 0, 1, 2,...$ are designated by the symbols, $\Sigma, \Pi, \Delta,...$)

Excited states,

$$K_1X_1 \qquad l_1 = 0, \quad l_2 = 0,$$
$$\lambda_1 = 0, \quad \lambda_2 = 0, \qquad s_1 = \tfrac{1}{2}, \quad s_2 = \tfrac{1}{2},$$
$$\Lambda = 0. \qquad\qquad S = 0, 1.$$
$$\therefore \text{ a } \Sigma \text{ term.} \qquad \therefore \text{ singlet or triplet.}$$
$$\therefore \text{ Terms :---}^1\Sigma, {}^3\Sigma.$$

$$K_1X_2 \qquad l_1 = 0, \quad l_2 = 1,$$
$$\lambda_1 = 0, \quad \lambda_2 = 0, 1, \qquad s_1 = \tfrac{1}{2}, \quad s_2 = \tfrac{1}{2},$$
$$\Lambda = 0, 1. \qquad\qquad S = 0, 1.$$
$$\therefore \Sigma \text{ or } \Pi. \qquad \therefore \text{ singlet or triplet.}$$
$$\therefore \text{ Terms :---}^1\Sigma, {}^3\Sigma, {}^1\Pi, {}^3\Pi,$$

$$K_1X_3 \qquad l_1 = 0, \quad l_2 = 2,$$
$$\lambda_1 = 0, \quad \lambda_2 = 0, 1, 2, \qquad s_1 = \tfrac{1}{2}, \quad s_2 = \tfrac{1}{2},$$
$$\Lambda = 0, 1, 2. \qquad\qquad S = 0, 1.$$
$$\therefore \Sigma, \Pi, \text{ or } \Delta. \qquad \text{singlet or triplet.}$$
$$\therefore \text{ Terms :---} {}^1\Sigma, {}^3\Sigma, {}^1\Pi, {}^3\Pi, {}^1\Delta, {}^3\Delta.$$

It may be interesting to compare these terms with those for the corresponding configuration in the helium atom, which contains, like the molecule of hydrogen, only two electrons.

TABLE II.

Comparison of Electronic Terms of He-atom and H_2-molecule.

Configuration.	Terms He-atom.	Terms H_2-molecule.
K_1K_1	$^1S_0$	$^1\Sigma$
K_1X_1	$^1S_0, \, ^3S_1$	$^1\Sigma, \, ^3\Sigma$
K_1X_2	$^1P, \, ^3P$	$^1\Sigma, \, ^3\Sigma, \, ^1\Pi, \, ^3\Pi$
K_1X_3	$^1D, \, ^3D$	$^1\Sigma, \, ^3\Sigma, \, ^1\Pi, \, ^3\Pi, \, ^1\Delta, \, ^3\Delta$

Thus acquainting ourselves with the process of calculating electron terms from the electron configurations, let us return to the explanation of Table I. Each horizontal row corresponds to the same total quantum number $n = 2, \, 3,...$(written at the beginning of each row), according as the excited electron is in the L, M, N,... levels, K_1 ($n = 1$) being the normal state of the molecule. Each row is divided into columns, as represented at the top by the l values 0, 1, 2,... (or by the letters s, p, d,...) of the excited electron according as it occupies X_1, X_2, X_3,... levels. The terms corresponding to any excited state of the molecule (with the given n and l) are written in the corresponding column by dividing the column into the requisite number of parts. The numbers 1, 3, written alternately along each row, represent the multiplicity (singlet or triplet) of a term.

Thus, for example, for the normal state of H_2 (K_1K_1), corresponding to $n = 1$ and $l = 0$, we have, as calculated above, only a $^1\Sigma$ term. It has been written in the corresponding position in the table as $1s^1\Sigma$, denoting by the prefix ($1s$) the K_1 state of the running electron. The absence of $1s^3\Sigma$ state (according to Pauli's principle) is supported by the fact that the H_2-molecule is diamagnetic.

For $n = 2$ there are two levels, L_1 and L_2. The respective electronic terms due to each configuration L_1, L_2 of the running electron are written at the head of each section in the respective columns $2s^1\Sigma$, $2s^3\Sigma$ for L_1, and $2p^1\Sigma$, $2p^3\Sigma$, $2p^1\Pi$, $2p^3\Pi$ for L_2.

For $n = 3$ there are three levels, M_1, M_2, M_3, and the same procedure as above is adopted in this case also.

Each electronic state consists of two distinct sets of molecules with non-intercombining systems of odd ($m =$

1, 3, 5,...) and even ($m = 0, 2, 4,...$) rotational levels. One set of molecules consists only of the odd rotational states, whereas the even rotational states are altogether missing in it ; while for the other set it is just the opposite. This splitting into two different sets arises from the conditions of symmetry and antisymmetry of the nuclear spin in the molecule, represented by the spin quantum numbers $S_p = 1$ and $S_p = 0$ respectively. For any given electronic state the transformation of molecules of one set ($S_p = 0$) into those of the other set ($S_p = 1$) are extremely slow, and therefore termed as 'non-intercombining.' In electronic transitions also this rule of combinations between the rotational levels is observed, namely, rotation levels with $S_p = 0$ for one electronic state will not combine with those with $S_p = 1$ for the other electronic state. The $S_p = 0 \leftarrow S_p = 0$ and $S_p = 1 \leftarrow S = 1$ transitions for the rotation levels only are allowed. Moreover, the $S_p = 1$ states are statistically about three times heavier than the $S_p = 0$ states. These assumptions, which are strongly justified by several experimental evidences (specific heat of hydrogen at different temperatures [14], Raman effect in liquid hydrogen [15], and spectroscopic evidences) [16], explain in a very elegant manner the alternation of intensities in lines of every band in the secondary spectrum of hydrogen, and also the facts why certain electron transitions give only the P and R branches, whereas others give the Q branch only. Thus, for example, taking the particular case of the Lyman and Werner bands, Lyman bands consist of P and R branches only, whereas the Werner bands consist of P, Q, and R branches, showing the alternation of intensity of the lines as predicted by Heissenberg. These facts are very conveniently explained with the help of the usual diagram used for the purpose.

For the ground ($1s^1\Sigma$) electronic state the odd rotation levels correspond to $S_p = 1$ and the even to $S_p = 0$, whereas for the B ($2p^1\Sigma$) state this is just the other way. It will be quite clear from the diagram observing the selection rules stated above for the combinations of the rotation levels, why only P and R branches are possible, and why the lines of these branches are alternately strong and weak. The C-level, which is the initial level $2p^1\Pi$ of the Werner bands, is double, with a and b sublevels. For $^1\Pi a$ there are odd rotation levels corresponding to $S_p = 0$, and even rotation levels for $S_p = 1$, whereas for $^1\Pi_b$ it is just the opposite. A careful inspection of the diagram will show clearly why transition $1s^1\Sigma \leftarrow 2p\Pi^1a$ gives P and R branches

while $1s^1\Sigma \leftarrow 2p^1\Pi_b$ gives the Q branch only. This doubling of levels belonging to the singlet system also is due to the uncoupling effect, so common and prominent in the case of the hydrogen molecule. Similar diagrams may be used for other bands also. The diagrams need no further explanation.

Now to resume the explanation of the table: the levels hitherto identified either definitely or provisionally have been indicated on the latest system of nomenclature, in their respective places in the table. The arbitrary names formerly attached to these levels have also been written, for the sake of convenience, in the top left corner of the corresponding sections of the columns. The figures in each
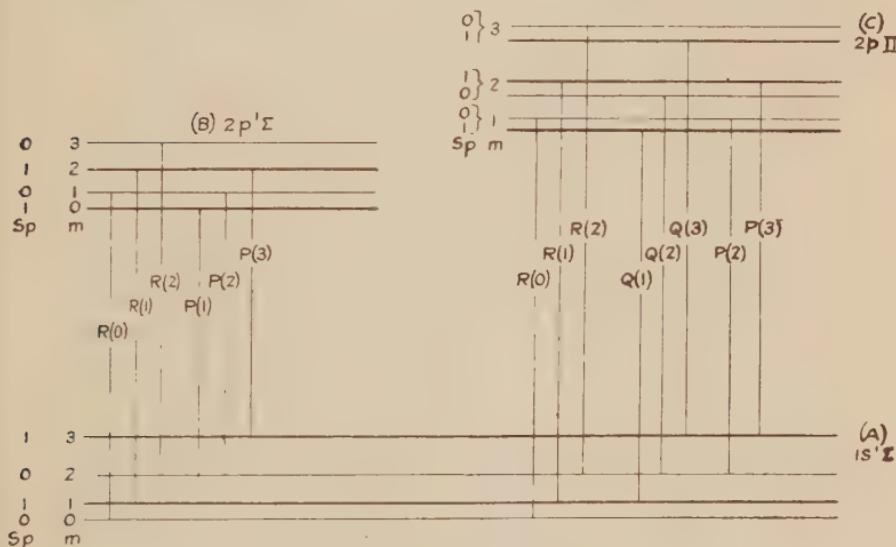
Alternating intensities in hydrogen spectrum
(Lyman and Werner bands).

section represent the electronic term values, and the vibrational and rotational frequency differences respectively for the corresponding electronic level. The levels which have been only provisionally identified have been marked (?). A few important band-systems have been indicated by dotted lines ending in arrows, showing the transitions between different electronic levels. For example, the

Lyman bands (A) $1s^1\Sigma \longleftarrow$ (B) $2p^1\Sigma$,

Werner bands (A) $1s^1\Sigma \longleftarrow$ (C) $2p^1\Sigma$,

and the Fulcher bands $2s^3\Sigma \longleftarrow$ $mp^3\Pi$ (according to Richardson)

are indicated in this manner. A comparison of this table
with Richardson's line diagram, showing the electronic
transitions for the different bands, will give a very clear idea
of the whole spectrum.

A detailed discussion has already been given by Richard-
son* in justification of the identifications of the electronic
levels made by him. A few suggestive remarks are, how-
ever, ventured in this communication. Richardson assigns
the $np^3\Sigma$ and $(n+1)p^3\Sigma$ levels without definiteness as
corresponding to either $n=2$ or 3. This is represented in
the table by thick arrows with a (?) at the end. From
the following considerations, however, it seems that the
levels may correspond more suitably to the value of $n=3$
than $n=2$. Comparing the energy values of the already
identified $2p$- as well as $2s$-levels with that of $np^3\Sigma$
level, it seems more probable that this $(np^3\Sigma)$ may be a
$3p^3\Sigma$, instead of a $2p^3\Sigma$ level. This leaves the $2p^3\Sigma$ level,
with an approximate value of about 48000, unidentified.
The existence of this level seems to be quite probable, as
otherwise it would be difficult from the already identified
levels to account for the lines at $\lambda\,3300$. This level may
also give intercombination bands with $1s^1\Sigma$ in the extreme
ultra-violet $(1s^1\Sigma \leftarrow 2p^3\Sigma)$, in the region $\lambda\,1300$ to 2000.
It will overlap the part of the Lyman bands up to $\lambda\,1600$,
and extend beyond to higher wave-lengths up to $\lambda\,2000$.
The bands may, however, be expected to consist of weak
progressions, and might possibly on that account have
escaped detection up to the present time. The 3^1K-level,
which, according to Richardson's statement, shows clearly
signs of a Σ-level, may possibly be identified as the $3s^3\Sigma$-
level. It forms a fairly proper Rydberg sequence to
$2s^3\Sigma$, and would readily combine with $2p$-terms. The
only objection that may be raised against this view is that
it gives a strong system of bands in combining with $2p^1\Sigma$,
whereas if it is a triplet $(^3\Sigma)$ level, this intercombination
may not ordinarily be expected to give such a strong system.
As, however, these points regarding the intensity of inter-
combination systems etc. have not yet been definitely
established in molecular spectra, this objection need not
be too seriously considered [16].

As regards the identification of the electron levels giving
rise to the Fulcher bands (also known as α, β, γ, δ bands)
and the Richardson's visible bands, which end on the
B-level of Dieke (the initial level of Lyman bands), there

* Transactions Faraday Soc. November and December 1929.

is a controversy which has reached no definite conclusion as yet. According to Richardson the Fulcher bands form a triplet system, $2s^3\Sigma \leftarrow mp^3\Pi_{a,\,b}$, whereas Finkelnburg describes them as singlet systems, $2s^1\Sigma \leftarrow mp^1\Pi_{a,\,b}$. On the other hand, Richardson's bands, ending on the B-level of Dieke, are supposed by Richardson to belong to the singlet system

$$2p^1\Sigma \longleftarrow 3d^1\Sigma$$
$$3d^1\Sigma,$$

whereas Finkelnburg considers it to be a triplet system

$$2p^3\Sigma \longleftarrow 3d^3\Sigma$$
$$3d^3\Sigma.$$

There are difficulties in accepting either of these views. Hund [17] has very clearly summarized the situation, showing the difficulties in deciding in favour of one view or the other. The point as to which view is correct still remains uncertain. Taking Richardson's view about the origin of these bands to be correct, great difficulty is experienced in trying to explain the fact that, whereas the singlet bands $2p^1\Sigma \to 3d^1\Sigma$, $^1\Pi$ show a rather complicated and abnormal structure of rotation levels, the Fulcher bands, which according to him are triplets, $2s\Sigma^3 \leftarrow mp^3\Pi$, and which therefore should be expected to show a much more complicated structure for the rotation levels, on the other hand show a normal and very simple rotation structure. If, on the other hand, Finkelnburg's view (which removes this above difficulty) be adopted, the Dieke's B-level must be identified as a $2p^3\Sigma$ level, which means that the Lyman bands are intercombination bands $1s^1\Sigma \leftarrow 2p^3\Sigma$. If so, then we must expect a very strong system of bands in the ultra-violet, corresponding to the singlet combinations $1s^1\Sigma \leftarrow 2p^1\Sigma$; but as yet no trace of such bands has been found. How can we explain this? It seems, therefore, that in the absence of further convincing evidence the present assignment of these levels is very indefinite and uncertain.

Out of the various possible electronic transitions (restricted by the usual selection rules) from $3d$ and $4d$, and also $2s$ and $3s$ levels to $2p$ levels, almost all have been located, mainly by Richardson. No band systems ending on $2p^3\Sigma$ in our table, or $2p^1\Sigma$ according to Finkelnburg, have been yet located. The discovery of band systems ending on the C- or the $2p^1\pi$-level is due to Richardson, and is published by him in a very recent paper *. The band system

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* *Loc. cit.*

$2s^3\Sigma\leftarrow-3p$, $4p^3\Sigma$ has also been identified by Richardson. The identification of 3^1Q, which is known to combine with B or $2p^1\Sigma$, giving only very weak progressions, has been made by Richardson as $3p^1\pi$. He thus seems to favour, as referred to above, the view that such forbidden transition as $\triangle k=0$ may be possible.

§ 2. *Classification.*

As stated in the Introduction, I have attempted identification of the lines of the forbidden transitions between Dieke's B-level $(2p^1\Sigma)$ and Richardson's 3^3P- or $(3p^3\pi)$-level—that is, $2p^1\Sigma\leftarrow-3p^3\pi$—transition. The full structures, vibrational as well as rotational, of the $3p^3\pi$ level (the initial level of the α-bands) were known from the classification of Richardson and Das, and those of the $2p^1\Sigma$ from Richardson and Davidson's[*] classification of visible bands ending on the $2p^1\Sigma$ (Dieke's B) level. Thus, having definite structures of the initial as well as final level for the system of bands I was seeking for, I attempted to classify lines forming these band systems. The result of this is given in the accompanying tables. This particular method of representation of the rotation structures of the band systems, though rather unusual and occupying more space, is, however, chosen, as it gives a more representative picture of the process. The duplicate nature of the Π-levels $(\Pi_a, \Pi_b$ having different energy values) is represented by the double structure in the tables. The P and R branches are due to $2p^1\Sigma\leftarrow3p^3\pi_a$ and the Q branches to $2p^1\Sigma\leftarrow3p^3\pi_b$ transitions. The relation

$$R(m) - Q(m) = Q(m+1) - P(m+1)$$

does not hold, as is the case with the α bands. All these features are clearly evident from the manner of representation of the bands. The initial double levels are marked as Π_a and Π_b. The tables are, however, not constructed to scale, so that though the difference $\Pi_a - \Pi_b$ increases with the values of m, the separations, as indicated in the tables, are of the same order. The same is true for the rotation frequency differences for the initial as well as for the final levels. The numbers written within brackets over the m's stand for the differences $F(m+1) - F(m-1)$ of frequency between the preceeding and following rotational energy values, as given by the analysis of Richardson and his co-workers. The tables inset within these tables are

[*] Loc. cit.

Rotation Structures.

TABLE III.

Final $2p\,{}^3\Sigma \longrightarrow$

$n''=0\ m$; $n''\to 0$

Initial $3p\,{}^3\Pi$	$n'=0\ m$:	0	(116·15) 1	(192·36) 2	(266·74) 3	(338·63) 4	(407·70) 5	6
		R'	**Q** 21673·48 (0)	**P'**				
Π_b / Π_a	1 {	21712·96 (1)		21596·48 (0)				
			(119·36)	(117·41)				
Π_b	(295·33) 2 {		21792·84 (0)	21713·89 (0)				
Π_a				(177·65)?	21599·87? (0)			
Π_b	(409·885) 3 {			(174·51)?	21774·38 (00)			
Π_a						21625·44 (0)		
						(228·83)		
Π_b	(521·05) 4 {				(235·68)	21854·27? (0)		
Π_a				21891·54? (0)	22010·06 (00)		21671·26 (2)	
Π_b	(627·95) 5 {							21738·57 (0)
Π_a								
Π_b	6 {							22298·78? (1)
Π_a								

Rotational Frequency Differences, Initial terms.

	Richardson and Dns.	Present Analysis.	Difference.
R'(1) − Q'(1)	119·12	119·36	0·24
Q(2) − Q'(2)	117·31	117·41	0·10
R(2) − Q'(2)	178·05	177·65	0·40
R'(2) − P'(2)	295·36	295·06	0·30
Q(3) − P'(3)	174·15	174·51	0·36
R(3) − Q'(3)	235·68	235·68	0·08
R(3) − P'(3)	409·89	410·19	0·30
Q(4) − P'(4)	229·32	228·83	0·49?
R(5) − P'(5)	627·95	627·52	0·43

Rotational Frequency Differences, Final levels.

	Richardson and Davidson.	Present Analysis.	Difference.
R'(0) − P'(2)	116·15	116·48	0·33
R'(1) − P'(3)	192·36	192·97?	0·61?
R'(2) − P'(4)	266·71	266·10?	0·61?
R'(3) − P'(5)	338·63	338·80	0·17

0 or 00. Lines with intensities greater than 1 or 2 rarely occur. A (?) mark is made before lines with intensity greater than 2. These large intensities may be due to blends, and therefore such lines need not be rejected

TABLE XIII. (*cont.*).

Vibration Frequency Differences.—Initial Level Q Branches.

m.	Richardson and Das.	Present Analysis.			
		$n''=0.$	$n''=1.$	$n''=2.$	$n''=3.$
($n'=0$——$n'=1$).					
1......	2240·21	2240·65?	—	—	—
2......	2234·23	—	—	—	—
3......	2225·28	2224·42?	—	—	—
4......	2213·44	2214·28?	—	—	—
($n'=1$——$n'=2$).					
1......	2114·84	—	—	—	—
2......	2109·09	—		—	—
3......	2100·38	—	2099·73?	2099·93	—
4......	2089·00	2089·24	—	2089·41	—
($n'=2$——$n'=3$).					
1......	1993·47	—	—	—	—
2......	1987·86	—	—	—	1987·89
3......	1979·50	—	—	—	1979·24
4......	1968·37	—	—	—	—
5......	1954·28	—	—	—	—

merely because they are strong. The progressions are also very weak. The 0–0, 1–0, 0–1, 1–2, 2–2, etc. progressions come out fairly complete ; the others are too weak to follow consistently, and only indications of their existence are available by the presence of isolated lines, as is evident from the tables. All these facts are quite consistent with what is to be expected in such transitions, which are ordinarily forbidden. It may be possible to explain the origin of a large number of lines by similar transitions.

TABLE XIV.

Vibrational Frequency Differences.—Final Levels.

	$m.$	Richardson & Davidson.	Present Analysis.			
			$n'=0.$	$n'=1.$	$n'=2.$	$n'=3.$
$(n''=0 \longrightarrow n''=1)$	0......	1318·34	R'−1318·26	-	—	—
	1......	1316·41	R'−1316·52		R'−1316·27	—
	2......	1312·55	P'−1312·55	—		—
	3..	1306·94	R'−1306·82 / P'−1306·18?	R'−1306·56 / Q−1306·13? / P'−1306 66	—	—
	4......	1299·68	Q−1299·28 / P'−1299·23	—	Q−1300·24? / P'−1300·22	—
	5......	1290 99	R'−1290·62	P'−1291·12		—
$(n''=1 \longrightarrow n''=2)$	0......	1281·47	R'−1281·35	—	R'−1281·36	—
	1......	1279·84	R'−1279·72	—	R'−1279·42 / Q−1279·06?	—
	2......	1276·60	P'−1275·56?	R'−1276·94 / Q−1276·53	R'−1276·24	—
	3......	1271·81		R'−1272·20 / Q−1271·98 / P'−1272·01	Q−1271·78	—
	4......	1265·59		- -	R'−1265·81 / Q−1265·50 / P'−1266·04?	—
	5......	1258·04	R'−1257·57?	P'−1258·18	R'−1257·82 / P'−1257·77	—
$(n''=2 \longrightarrow n''=3)$	0.. ...	1246·71	- -	—	R'−1246·65	-
	1......	1245·25	—	—	—	—
	2......	1242·38	P'−1243·20?	=	—	—
	3......	1238·12	-	—	R'−1237·23? / Q−1237·42?	—
	4......!	1232·61	—	—	R'−1233·12	—
	5......	1225·89	P'−1225·01?		R'−1225·98 / Q−1226·27 / P'−1226·13	—

Table XII. gives a list of such lines referred to above as forming isolated members of very weak progressions; separate tables for representing the rotation structures of such very weak progressions consisting only of isolated lines are not constructed. Tables XIII. and XIV. are constructed to give the vibrational frequency differences for the initial as well as the final levels. The tables require little explanation. It may be observed that these figures compare fairly well (generally within 0.5 cm.$^{-1}$) with the corresponding values obtained in their analysis by Richardson and his co-workers, as will be clear from these tables.

In conclusion, I wish to record my sincerest thanks to Prof. M. N. Saha, F.R.S., for his valuable suggestions and guidance throughout this investigation.

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LXVII. *On the Charge Distribution and Diamagnetic Susceptibility of Atoms and Ions.* By G. W. BRINDLEY, *M.Sc., Assistant Lecturer in Physics at the University of Leeds* *.

ABSTRACT.

THE diamagnetic susceptibilities calculated by Pauling for hydrogen-like atoms and by Stoner using Hartree's distributions of charge are generally larger than experimental

values. Slater has given a method for calculating approximate wave-functions which yields susceptibilities in much better agreement with experiment. The deduction of ionic susceptibilities from measurements made on salts is briefly considered.

1. *Introduction.*

THE diamagnetic susceptibility of an atom is closely related to its distribution of charge, and when the distribution is spherically symmetrical the susceptibility can easily be calculated. A comparison of calculated values with experimental results gives a test of the charge distributions which, as Stoner [1] has pointed out, may supplement that given by the X-ray scattering curves, for whereas the scattering power of an atom for X-rays depends mainly on the electrons near the nucleus, the diamagnetic susceptibility depends mainly on the outer group of electrons.

2. *A Comparison of Diamagnetic Susceptibilities calculated by Pauling and by Stoner, with Experimental Results.*

The diamagnetic susceptibility, χ, of a symmetrical atom is given by [2]

$$\chi = -\frac{e^2}{6mc^2}\Sigma\overline{r^2}, \quad \cdots \quad (1)$$

where $\overline{r^2}$ is the mean square distance of an electron from the nucleus, the summation extending over all the electrons. Pauling [3] and Van Vleck [4] have shown independently that $\overline{r^2}$ is connected with the quantum numbers n and l for a single electron in the field of a nucleus of charge $(Z-s)e$ by the relation

$$r^2 = \frac{n^2}{(Z-s)^2}\left\{\frac{5}{2}n^2 - \frac{3l(l+1)-1}{2}\right\}, \quad \cdots \quad (2)$$

$\overline{r^2}$ being given in terms of a_0, the radius of the one quantum orbit of hydrogen ($a_0 = 0.532 \times 10^{-8}$ cm.). Pauling estimated the screening constant s for different electron groups in atoms and ions containing many electrons, and so calculated a large number of susceptibilities. His results are compared with experiment in Table I.

Stoner [1] has more recently calculated $\overline{r^2}$ from the charge distributions obtained by Hartree's method [5]. In Hartree's

notation $\left(\dfrac{dZ}{dr}\right)$ is the radial charge density in electrons per unit radial distance. Then

$$\overline{r^2} = \int_0^\infty r^2 \left(\frac{dZ}{dr}\right) dr \Bigg| \int_0^\infty \left(\frac{dZ}{dr}\right) dr, \quad . \quad . \quad . \quad (3)$$

and, as the lower integral is equal to the number of electrons in the atom, we have from (1) for the gramme atomic susceptibility, X_A,

$$X_A = -0.807 \times 10^{-6} \int_0^\infty r^2 \left(\frac{dZ}{dr}\right) dr. \quad . \quad . \quad (4)$$

Since the charge distributions are calculated for *free* atoms and ions, a comparison between experiment and theory can only be made strictly for the rare gases. Stoner found a good agreement in the case of helium, but was unable to extend the comparison to neon and argon, the charge distributions not having then been calculated. These have now been obtained *, and the results are given in Table I.; it is seen that the agreement is not good for neon and argon.

In comparing ionic susceptibilities there is some uncertainty in the "experimental" values, because these have to be estimated from measurements made on salts, but in general the uncertainty is not large; this point is discussed later.

The experimental and calculated susceptibilities are compared in Table I. Pauling's results are given in the second column, and in the third column are the results obtained from Hartree's charge distributions, those calculated previously by Stoner being marked (S). In the fifth column are the results of Wills and Hector [6] for the rare gases, and under A a set of values for the ions is given obtained by a method described later, and under B the mean of a series of values recently published by Weiss [7].

For helium and the smaller positive ions the agreement between theory and experiment is satisfactory, but for neon and argon and the diffuse negative ions the agreement is not good.

Since the susceptibility depends mainly on the outer electron groups it seems probable that some of the discrepancy between theory and experiment is due to the

* I am indebted to Prof. Hartree for the charge distributions for neon and argon. The distributions for F^- and Ca^{+2} have been previously calculated by the writer. The value given in Table I. for Mg^{+2} was obtained by interpolating between Ne and Na^+, and Al^{+3} and Si^{+4}, these distributions having all been calculated by Hartree's method.

calculated charge distributions being too diffuse for the outer electrons. It is also possible that the charge distributions for ions in solution may be less diffuse than for free ions.

TABLE I.

Values of $-\chi_A . 10^6$.

	Pauling.	Hartree.	Slater.	Experimental values.	
Helium ..	1·54	1·90 (S)	1·68	1·88	Wills and Hector.
Neon	5·7	8·81	5·7	6·7	
Argon	21·5	25·3	18·8	18·1	
				A (present method).	**B** (Weiss mean values).
F⁻	8·1	17·3	8·3	—	...
Cl⁻	29·0	40·4 (S)	25·8	24·0	23·1
Br⁻	54	—	40·1	37·5	34·1
I⁻	80	—	59·8	55·7	50·2
Li⁺	0·63	0·70 (S)	0·67	0·7	—
Na⁺.........	4·2	5·74 (S)	4·2	5·2	8·0
K⁺	16·7	17·6 (S)	14·4	13·5	16·2
Rb⁺	35	30·1 (S)	25·8	24·0	24·3
Cs⁺	55	—	39·5	36·8	38·0
Mg⁺²	3·2	4·3	3·2	3·8	5·15 to 8·0
Ca⁺²	13·3	13·4	11·4	10·8	11·4
Sr⁺²	28	—	21·5	19·5	19·7
Ba⁺²	46	—	33·2	30·0	—

3. *Slater's Method of Estimating Charge Distributions.*

Slater [8] has recently published an account of a method by which approximate wave functions may be calculated for atoms and ions. Zener [9] had previously shown that the nodes in the wave function are unimportant, and Slater therefore takes for the wave function of an electron in a symmetrical atom

$$\psi = r^{(n^*-1)} . e^{-\left(\frac{Z-s}{n^*}\right)r}, \qquad . \quad . \quad . \quad (5)$$

n^* being the effective principal quantum number and $(Z-s)$ the effective nuclear charge. Slater gives rules, based on energy considerations, by means of which n^* and s can be

obtained very easily for any electron group, the groups being as follows:—$1s$; $2s, p$; $3s, p$; $3d$; $4s, p$; $4d$; $4f$, etc.

The radial electron density is $4\pi r^2 |\psi|^2$, whence

$$\overline{r^2} = \int_0^\infty r^4 |\psi|^2 dr \bigg/ \int_0^\infty r^2 |\psi|^2 dr$$
$$= (n^*)^2(n^* + \tfrac{1}{2})(n^* + 1)/(Z-s)^2. \quad . \quad (6)$$

Slater shows that for helium, neon, and argon $\overline{r^2}$ calculated from (6) agrees well with $\overline{r^2}$ calculated from the diamagnetic susceptibilities. It was therefore thought worth while to extend the comparison to all atoms and ions for which experimental data are available.

Values of $-\mathcal{X}_A \times 10^6$, calculated from Slater's charge distributions, are tabulated in the fourth column of Table I., and in almost all cases they agree well with experiment.

4. *On the Deduction of Ionic Susceptibilities from Measurements made on Salts.*

The susceptibilities of ions cannot be measured directly, but have to be deduced from measurements on salts either in solution or in the crystalline state. If an additive law can be assumed, then it is only necessary to deduce the susceptibility of one ion in order to obtain the remainder. Joos [10] and Ikenmeyer [11] have obtained sets of ionic susceptibilities by starting from CsI, which in solution forms Cs^+ and I^- ions, each with a xenon-like arrangement of electrons and with nuclear charges 53 and 55. They assumed the ionic susceptibilities to be inversely proportional to the squares of the nuclear charges, and hence Ikenmeyer obtained for Cs^+, $\mathcal{X}_A = -45.75 \times 10^{-6}$, and for I^-, $\mathcal{X}_A = -49.25 \times 10^{-6}$. This procedure does not seem to be justifiable.

Table II. shows how the different electron groups in Cs^+ and I^- contribute towards the total diamagnetism of these ions according to Slater's scheme. The outer electron groups, the $5s$ and $5p$ groups, contribute roughly 70 per cent. of the total in each case. It seems clear that the ionic susceptibilities should be taken inversely proportional to $(Z-s)^2$, *i. e.*, to the squares of the *average effective* nuclear charges. We then obtain, from Ikenmeyer's result, for Cs^+, $\mathcal{X}_A = -37.8 \times 10^{-6}$, and for I^-, $\mathcal{X}_A = -57.2 \times 10^{-8}$. In exactly the same way we might start from KCl, which in

solution forms argon-like ions, or from RbBr, which in solution forms krypton-like ions.

Weiss[7] has deduced a set of ionic susceptibilities in a slightly different way by starting from the observed value for HCl. Weiss points out that just as the optical refractivity of solutions is influenced by the effect of the charged ions on water molecules, so the susceptibilities of salts in solution will be influenced in a similar way, and he estimates the magnitude of this effect. It is found to be

Table II.

Contributions of different electron groups to the suscepti-bilities of Cs^+ and I^-, and the corresponding values of $(Z-s)$, from Slater's data, *l. c.*

Electron groups.	Cs^+.		I^-.	
	$-\Delta\chi_A \times 10^6$.	$(Z-s)$.	$-\Delta\chi_A \times 10^6$.	$(Z-s)$.
$3s, p$	0·4	43·7	0·5	41·7
$3d$	0·9	33·8	1·0	31·8
$4s, p$	2·3	27·2	2·7	25·2
$4d$	8·7	15·8	11·4	13·8
p	27·1	$9·2_5$	44·2	$7·2_5$
	$\Sigma, 39·4$		$\Sigma, 59·8$	

most important for small ions, H^+, Li^+, Mg^{+2}, Ca^{+2}, and unimportant for large ions. A disadvantage of Weiss's method is that the results depend on the value chosen for χ_A for Cl^-, and this depends on the correction which has to be made for the presence of H^+ ions in HCl. Weiss calculates susceptibilities separately from the measurements of Hocart, Reicheneder, and Pascal. In Table I. average values only are given.

Ikenmeyer[11] has made an extensive series of measure-ments on salts in solution. His method of estimating ionic susceptibilities appears to be unsatisfactory, for reasons already given. A new set of values has therefore been deduced by starting from CsI and assuming the sus-ceptibilities of Cs^+ and I^- to be inversely proportional to the squares of the average effective nuclear charges. For CsI it is unnecessary to make any correction for the effect

of the ions on water molecules. When the corrections calculated by Weiss are applied, where necessary, to Ikenmeyer's results a set of ionic susceptibilities can be obtained, which is consistent with the experimental results and which is also in satisfactory agreement with the values calculated from Slater's distributions of charge.

The "experimental" values are tabulated in the fifth column of Table I. ; under A values obtained by the present method are given, and under B are the average values of Weiss, since the two sets agree moderately well, the uncertainty in either set is probably small. For Mg^{+2} and Na^+ the values given by Weiss are almost certainly too large.

5. *Summary.*

The close connexion between the diamagnetic susceptibility and the distribution of charge of symmetrical atoms is briefly described. Susceptibilities calculated by Pauling and by Stoner, using Hartree's distributions, are generally larger than the experimental results. Slater has given a method of calculating charge distributions which, though not so satisfactory as Hartree's method theoretically, gives susceptibilities in fairly close agreement with experiment.

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   Nov. 1930.

LXVIII. *Early Developments of A.C. Theory.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

OBJECTION must be made to Mr. Windred's conception (or knowledge) of early American (U.S.) or early English history of the teaching of A.C. Theory. Those acquainted with John Perry's textbooks on the 'Calculus for Engineers' and the 'Steam Engine' will doubtless be astounded at the statement of English neglect.

Perhaps Mr. Windred does not know that John Perry's operational applications to electrical circuit theory are much more general than those that were employed by C. P. Steinmetz and others. Heaviside operators are complex and "supercomplex" at one and the same time. As a matter of fact the more general theory due to Heaviside (and exemplified by Perry) was first taught officially at one of the universities of the United States by the writer as far back as 1917, using John Perry's text as a basis.

The applications, however, of complexes to the more difficult problems of the iron losses in transformer plate (1915) only found hospitable ground in England. This work antedates that of Latour (Marius) on radio frequency effects. As for the first proof of Heaviside's Expansion Theorem depending on the generalized expansion in terms of partial fractions, which, by the way, antedated Carson's original work, this found similar treatment, and finally led to its publication in France with a kindly translation and comment by Prof. Pomey.

The turn in American affairs appeared to have occurred shortly afterwards, for a whole list of applications by the writer to general A.C. Theory was later sympathetically published by the University of California as one of their 1918 'Engineering Publications.' This early work, however, is not mentioned in Mr. Windred's list. The most notable oversight is with regard to the concept of complex inductances and capacitances. Applications to A.C. Theory at radio frequencies again found hospitable ground rather in English technical journals (Journ. I.E.E.). Radiation of energy from an antenna cannot be obtained except by the use of complex reactances (or complex

L's and C's). Then there are the writer's applications of "supercomplexes" to Eigenwerthe etc., and to Schrödinger's Wave Theory. For history should be history.

<div style="text-align: right">Yours faithfully,

A. PRESS.</div>

561 W. 140th Street,
    New York, U.S.A.
Nov. 21, 1930.

LXIX. *Notices respecting New Books.*

The Physical Principles of Electricity and Magnetism. By R. W. POHL, Professor of Physics in the University of Göttingen. Translated by WINIFRED M. DEANS, M.A., B.Sc. [Pp. xi+356, with numerous figures.] (London and Glasgow : Blackie & Son, Ltd., 1930. Price 17s. 6d. net.)

THIS volume is intended for students of science and engineering with, presumably, a very slight knowledge of mathematics. The author's aim has been to make the relationships between experimental facts clear and to give the reader an idea of the wide range of modern electrical theory. The treatment is essentially experimental and graphical, and the experiments are carefully selected for their theoretical implications. A feature of the volume is the large number of excellent diagrams and illustrations. The whole field of modern electrical theory is covered, and a student who has worked through the experiments described, in conjunction with the study of the text, should have a very clear grasp of all the physical principles involved.

The Spirit of Chemistry : an Introduction to Chemistry for Students of the Liberal Arts. By Prof. ALEXANDER FINDLAY. [Pp. xvi+480, with numerous portraits and illustrations and 88 text-figures.] (London : Longmans, Green & Co., 1930. Price 10s. 6d.)

THE keynote of this volume is contained in the quotation from Samuel Brown, given on the titlepage : "It is not the particular facts of a science that constitute its vitality, but the generic facts or conceptions to which they have elevated the mind. Facts are the body of science and the idea of those facts is its spirit." The volume is not intended primarily for the student of chemistry, but for those who, whilst not

interested in science as a career, wish to learn something of the fundamentals, principles and concepts, and of the history of a science which is of great importance to modern civilization.

The author has succeeded well in his task and has produced a volume of great interest. The historical development of the subject is outlined and brief biographical sketches of great chemists of the past are given. The volume ranges over the whole range of chemical science—physical, inorganic, and organic—and the fundamental principles are kept well to the front. Practical applications and industrial methods are described and the great part which chemistry plays in everyday life is made apparent. The volume cannot fail to promote a better understanding of the debt which modern civilization owes to science.

The Selenium Cell: its Properties and Applications. By G. P. BARNARD, with a Preface by J. W. T. WALSH, M.A., D.Sc. [Pp. xxix +331, with 258 figures.] (London : Constable & Co., 1930. Price 35s. net.)

THE light-sensitive properties of selenium were discovered in 1873 by Willoughby Smith, and since that date these properties have attracted wide attention and have formed the basis of an extraordinarily large number of inventions, many of which have proved more ingenious than practical. The literature bearing on the subject is very extensive and scattered, and, moreover, the results of different investigations not infrequently appear to be contradictory, due to the fact that the behaviour of selenium depends to a large extent upon its previous history.

A detailed and critical survey of the available material was much to be desired, but the magnitude of the task might well have deterred the boldest author. Mr. Barnard, of the Electricity Department of the National Physical Laboratory, has tackled it with conspicuous skill and success, and there is little doubt that this volume will long remain the standard work on the properties and applications of selenium. Workers in this field can now ascertain exactly what has or has not been done in any particular direction without having to search through a maze of literature.

A complete bibliography of the subject is given, and with few exceptions the author has consulted every reference in order to verify its correctness.

The volume is divided into two parts. The first deals with the properties of selenium, chemical and physical, with the construction of selenium cells, and with the various theories of the action of light on selenium. The material has been critically examined and the reasons for the apparent dis-

cordant results obtained by different experiments are explained.
The second part deals with the practical applications of
selenium, which are extraordinarily varied. Numerous
general applications are first considered, and then several
of the more important applications are dealt with in greater
detail — the applications to photometric measurements,
to the optophone and light-telephony, to talking films and
television.

Valuable tables of the mechanical, thermal, optical, and
electrical constants of selenium are given in appendices.
The volume is provided with numerous figures and illus-
trations. Attention must be drawn to the excellence and
completeness of the index, which is a model of what an index
should be.

A Textbook of Practical Physical Chemistry. By K. Fajans
and J. Wüst. Translated from the German by Bryan
Topley. With a Preface by F. G. Donnan, LL.D., F.R.S.
[Pp. xv+234, with 74 figures.] (London : Methuen & Co.,
Ltd., 1930. Price 15s. net.)

The authors of this volume have had wide experience both in
experimental investigation and in the training of students.
The volume is based on a course of instruction in use in the
chemical laboratory of the University of Munich. It is
planned on somewhat unusual lines, the theory of each experi-
ment being given first and then the practical details, which
are in great detail, so that the practical work can be carried
out with a minimum of assistance. In this way the theoretical
points, which must be clearly grasped by the student if the
experiment is to be intelligently performed, can be stressed
and self-reliance in experimental work is developed. Special
attention is devoted to theoretical and practical details
which the experience of the authors has shown to involve
difficulties for the student.

The introduction is full of advice of the greatest practical
importance on matters often ignored by the student. The
assessment of the precision of measurement of the various
observational quantities and of the effect of error in each
one on the quantity which is to be evaluated is explained,
and the uselessness of proceeding to unnecessary accuracy
in the measurement of quantities whose effect on the final
result is small is pointed out.

The book covers a wide field and a varied range of apparatus.
It includes experiments in spectrophotometry and ultra-
violet spectrography, the use of refractometers, the determina-
tion of hydrogen ion concentration, the measurement of
electromotive force, including descriptions of several types

of cell, metallography and the preparation of sections, radio-activity, and many other subjects. Where special instruments are used these are described and their theory given.

With such a textbook as a guide the student should be able to work with understanding and to acquire considerable practical skill in the use and manipulation of instruments. Detailed references to standard works are given throughout, so that the student can obtain fuller information on the theoretical side. Prof. Donnan states in his preface that this textbook will be used in the chemical laboratory of University College, London.

Applications of Interferometry. By W. Ewart Williams, M.Sc. With a Preface by O. W. Richardson, F.R.S. [Pp. viii+104, with 43 diagrams.]
Photochemistry. By D. W. G. Style, Ph.D. With a Preface by A. J. Allmand, M.C., D.Sc., F.R.S. [Pp. vii+96, with 8 figures.]
    [Methuen's Monographs on Physical Subjects. (London: Methuen & Co., Ltd., 1930. Price 2s. 6d. each net.)]

The busy worker in science will welcome this series of monographs, containing brief but accurate accounts of recent work in and the present position of the subjects which are dealt with. The various branches of science are becoming to an increasing extent interdependent, but the present rate of output of original papers makes it more and more difficult for a worker in one branch to keep in as close touch as is desirable with the developments of other branches. These monographs provide a valuable introduction to recent work. A feature of importance in each volume is a selected list of references, which will enable the reader to pursue any particular point in greater detail.

Mr. Williams has given an excellent account of the principles of interferometry, of the various forms of interferometer, and of many practical applications. The applications are so numerous that it has been possible to include a selection only, chosen for their interest and importance. These embrace both purely scientific and also technical applications. A broad division of interferometers into two classes is made : those in which interference is caused by division of wave-front and those in which it is caused by division of amplitude. The latter possess the great advantage that extended light sources can be used, and consequently brighter fringes in general obtained. The two classes are considered separately. A special chapter is given to the Michelson interferometer and its applications. Interferometers which involve the simultaneous division of both amplitude and wave-front are then

considered. The most important of this type is the Twyman and Green modification of the Michelson interferometer, which has important applications for optical testing. A final chapter deals with interference effects from multiple beams.

Photochemistry is a branch of chemistry which owes much to modern physical theories. It promises in return to assist the physicist in the understanding of various molecular phenomena. Under the term photochemistry is included the study of the reactions induced by light. The phenomena which occur when radiation is absorbed by matter depend upon the circumstances, the properties of the excited molecule or atom, and the size of the quantum of radiation. If the quantum is large an electron may be expelled ; when not large enough for this to occur the molecule may or may not be dissociated into atoms. The activated molecule or atom can undergo reactions which would not be possible for a normal atom. In this monograph the subject is treated in broad outline, especially suitable for physical readers, and a number of illustrative reactions are discussed in detail. The conception of chain reactions is carefully explained ; the practical application to the combustion of volatile fuels is first discussed. Homogeneous one-component systems, homogeneous binary systems of variable mass and composition, and homogeneous *n*-component systems are considered in succession. A discussion is then given of strain and stress, leading to the consideration of the thermodynamical treatment of systems homogeneously strained and the stress-strain relations for isothermal changes of state. Systems not in equilibrium and irreversible processes are finally considered. The introduction forms a valuable addition to the publication.

A complete index is given at the end. A word of commendation of the excellence of the printing is due.

Methods of Correlation Analysis. By M. EZEKIEL. (New York : John Wiley & Sons, 1930. Price 22*s*. 6*d*. net.)

THIS book deals not with the whole field of statistics, but rather with that part of the field which is concerned with studying the relations between variables. The author's aim is throughout to show how the various standard methods may be employed in practical research work, what their limitations are, and what the results really mean. The examples which are used in presenting the methods are drawn very largely from the author's own field of work in agricultural economics, but he has been careful to demonstrate them in terms sufficiently general to allow their application to any suitable field. This book is to be heartily recommended.

Electrolytic Conduction. By F. H. NEWMAN. (London : Chapman & Hall, 1930. Price 25s. net.)

THIS book is designed primarily for the physicist, but will be of interest to all those who are interested in the conduction of electricity through electrolytic solutions. Its appearance is to be welcomed, as during the past ten years the theory of electrolytic conduction has been remodelled and has become of the first importance in the technical applications of electro-lytic processes. The book is a notable achievement, since it gives a full and systematic survey of the modern theory of the complete ionization of electrolytic solutions, and con-tains, in addition, very full references which will prove of great value to the advanced student.

LXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 456.]

December 17th, 1930.—Prof. E. J. Garwood, M.A., Sc.D., F.R.S., President, in the Chair.

Dr. HAROLD JEFFREYS, M.A., F.R.S., delivered a lecture on 'The Mechanics of Mountains.'

The Earth's upper crust in the continents appears from seismology to consist of three layers, an upper one of granitic constitution, about 10 km. thick, an intermediate one about 20 km. thick, the properties of which fit tachylyte, and a lower one probably of dunite, extending half-way to the centre of the Earth. Above the granitic layer is the sedimentary layer, with an average thickness of probably about 2 km., but considerably thicker in special regions. The outflow or inflow involved in maintaining isostatic compensa-tion is in the lower layer, but at a smaller depth than 50 km.

The mechanical properties of the outer crust indicate that the crustal shortening in a major epoch of mountain - formation should be of the order of 40 km. The actual height and extent of the great ranges correspond to a shortening of about 60 km. This estimate is arrived at by considering what elevation would be produced if the light upper layers were compressed by a given fraction of their original length and enough outflow in the dense lower layer took place to restore isostasy.

This estimate is much less than the horizontal movement observed in the field, and it is suggested that the only possible explanation is that the horizontal movement is a surface-phenomenon almost

confined to the sedimentary layer, and caused by the crustal shortening, but not equivalent to it.

It appears that prolonged deposition of sediments leads to an obstruction of the normal outflow of heat from the Earth, and hence to an increase of temperature and a reduction of strength through a depth of the order of 100 km., thereby localizing the yield when the stresses due to contraction of the interior become too great for the strength of the outer crust to withstand. The immediate result of a local failure would be a local elevation so high that the heated sediments would proceed, as a secondary effect, to flow out horizontally under gravity and give a series of flat folds closely resembling the observed nappes. Explanations of 'back-folding' and of the gneissic core of a great mountain-system appear to follow naturally.

Emphasis is laid on the importance of recognizing the intermediate layer in discussions of the mechanics of geological processes. Isostatic readjustment can take place by horizontal outflow in this layer as in the lower layer, though much more slowly, and it seems that this process may play an important part in the formation of geosynclines and the levelling of old mountain-systems.

Obituary Notice.

WE regret to announce the death on February 13th of RICHARD TAUNTON FRANCIS, one of the Editors of the 'Philosophical Magazine' and of the 'Annals and Magazine of Natural History,' at the age of 47. He was the younger son of the late Dr. William Francis, and was educated at St. Paul's School and afterwards at Göttingen University, where, however, his studies were cut short by a very serious cycling accident. On the death of Dr. Francis in 1904 he became a partner in the firm of Taylor & Francis with his brother, the present William Francis, until the retirement of the latter in 1917. Although he had been in bad health for some time preceding his death, he appeared to be regaining strength, but a sudden attack of influenza proved fatal. He leaves a widow and one son.